ELECTRON IMPACT STUDIES ON HALOGEN CONTAINING MOLECULES.

Thesis Submitted for
the Degree of Doctor of Philosophy

at

Glasgow University

by

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July, 1959.

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SUMMARY.

The work described in this thesis has been divided into three sections, namely:

1. "The Latent Heat of Sublimation of Carbon and the Heat of Dissociation of Nitrogen."
2. "The Mass Spectra of Camphor and Some of its Halogen Derivatives."
3. "Electron Impact Studies on some Chlorinated Benzaldehydes."

In Section 1 a study of the ionization and dissociation of the molecules CX_4 ($X \equiv F, Cl, Br$); CHX_3, CH_2X_2, CH_3X ($X \equiv Cl, Br$) and NH_3 was undertaken. Appearance potentials of some of the positive ions produced under electron bombardment were obtained for each compound, while a suitable method was devised for the generation of some of the corresponding free radicals and the measurement of their ionization potentials. Dissociation processes were then selected to account for the formation of each ion. Combination of the experimental data in the appropriate equations then gave a series of bond dissociation energies from which the heat of atomization of each compound was obtained. Substitution of this heat of atomization in a suitable thermochemical cycle then allowed a value for the latent heat of carbon (L_c) or the heat of dissociation of nitrogen, $D(N_2)$, to be estimated. From the results it was conduded that L_c = 7.386 eV., and $D(N_2)$ = 9.756 eV. are most likely to be correct.

In Section 2, the "Cracking Patterns" of camphor, α-bromo-, α-chloro-, β-bromo-, β-iodo-, α:α- dibromo- and α:β- dibromo camphors are recorded. An attempt was then made to explain the occurrence of the principal peaks of each spectrum in terms of the current theories of the origin of mass spectra and to interpret the differences in the spectra of the seven compounds with the variation in molecular structure. This has been fulfilled with

some modicum of success. Plausible mechanisms, based on such generalizations as facile allylic bond fission, ready elimination of CO and the occurrence of rearrange-:ments promoted by the relative stabilities of the frag-:ment ions, have been proposed for the production of the more prominent ions observed. It is emphasized that the results of the present work can only give an indication rather than a conclusive proof of the behaviour of the camphor skeleton under electron impact.

In Section 3, the appearance and ionization potent-:ials of some of the ions produced in the electron impact induced dissociation of o-, m- and p- chlorobenzalde-:hydes are recorded. The dissociation energies of the bond between CHO and the aromatic nucleus, D(Ar-CHO), was measured in each case, and compared with that of ben-:zaldehyde itself. It was then possible to interpret the results in terms of the Inductive and Conjugative effects of the substituent chlorine atom. The dissoc-:iation energies of the corresponding bond in the mole-:cule ion, $D(Ar^+-CHO)$, were also obtained. The relation-:ship between D(Ar-CHO) and $D(Ar^+-CHO)$ was discussed, resulting in the tentative proposal that a benzaldehyde type molecule ion may undergo ring expansion to give an ionized derivative of tropone.

SECTION 1.

The Latent Heat of Carbon and the Dissociation Energy of Nitrogen.

The question of the allocation of a correct value to the latent heat of sublimation of carbon and the heat of dissociation of nitrogen has been the object of much research and controversy over the past thirty years. For references prior to 1945, a review article by Long and Norrish (1) may be consulted; while monographs by Gaydon (2a), Herzberg (3a), Field and Franklin (4a) and Cottrell (5a) give good accounts of recent thought on the matter.

The latent heat of sublimation of carbon, i.e. the heat of formation of monatomic carbon gas (at 298°K and constant pressure) from graphite, will be denoted by the symbol L_c; while $D(N_2)$ will represent the heat of dissociation of nitrogen. The quantities L_c and $D(N_2)$ are not independent, but are related to one another by means of the thermochemical cycle;

$C(s) + \frac{1}{2} N_2(g) \longrightarrow CN(g)$	$-\Delta H_f(CN)$
$C(s) \longrightarrow C(g)$	L_c
$\frac{1}{2}N_2(g) \longrightarrow N(g)$	$\frac{1}{2}D(N_2)$
$C(g) + N(g) \longrightarrow CN(g)$	$-D(C-N)$

whence $L_c + \frac{1}{2}D(N_2) - D(C-N) + \Delta H_f(CN) = 0$

$\Delta H_f(CN)$ is known to be 4.16 eV. (4b) and D(CN) = 8.2 eV. has been measured by Carroll (65). Hence knowledge of either L_c or $D(N_2)$ permits the other to be calculated.

Since 1945 four values for L_c have been put forward by various authors (2a). The estimates, 125.0, 138.5, 141.3 and 170.4 K.Cal/Mole are much too diverse to be acc-:ounted for solely by experimental error. A short acc-:ount of the various methods used to obtain these results will be given together with such critisms as have been put forward from time to time.

Values of L_c may be arrived at by two general methods: (a) by direct measurement of the vapour pressure of mon-:atomic carbon in equilibrium with graphite at various temperatures, or (b) by the determination of the heat of atomization of a carbon containing compound of known heat of formation - whence L_c may be deduced by a suitable thermochemical cycle.

(a) Direct Methods

Since carbon has a low volatility, there is a res-:triction in the methods available for the measurement of vapour pressure. Two of those are the Knudsen (5b) and Langmiur (6) methods. The Knudsen system depends on the measurement of the rate of effusion of the vapour into a vacuum from a small hole in the wall of a heated tantalum cell containing the solid material; while the Langmuir method involves the measurement of the rate of evaporation into a vacuum of the solid material (usually in the form

of a heated filament) per unit of area. In both types of experiment, the mass spectrometer has been used to id-:entify the gaseous species present.

The Langmuir method was applied to the evaporation of graphite by Marshall and Norton (7) who, assuming that all the vapour present consisted of monatomic carbon, ded-:uced that L_c= 175K.Cal/Mole. Chupka and Inghram (8,9) and Honig (10) examined the vapour from a heated carbon filament by means of a mass spectrometer. They found app-:reciable quantities of C_2 and C_3 entities present as well as C, but from the dependence of the C^+ ion intensity with temperature, Chupka and Inghram proposed L_c= 176K.Cal. in good agreement with Marshall and Norton.

Herzberg, who favoured (on spectroscopic grounds) the smaller value for L_c of 125K.Cal., critised these results. He and his co-workers (11) propounded a theory, based on the atomic structure of graphite, stating that the true heat of vaporization was only about three quarters of the experimental value, which would reduce Chupka and Inghram's result to about 130K.Cal. Herzberg's theoret-:ical treatment has been critised in turn by Kynch and Penney (12) on the grounds that Herzberg had oversimplified the problem for quantitative evaluation. More recently Hoch and his collaborators (13) have repeated Chupka and Inghram's experiments using graphite, tantalum carbide (TaC) and tungsten carbide (WC). TaC and WC have differ-

:ent molecular structure to that of graphite hence Herz-:berg's theory cannot be applied to them, while all three compounds produce values of L_c = 170.K.Cal.

The Knudsen effusion method was initially employed by Brewer, Gilles and Jenkins (14) who, using hole area-internal surface area ratios of 1:250 and 1:600, obtained results compatible with L_c = 170K.Cal. On the other hand, similar measurements by Doehaerd, Goldfinger and Wael-:broek (15), using a much wider range of hole area - sur-:face area ratios, decided their results best suited L_c = 142K.Cal. These conclusions of Doehaerd were founded on the assumption that the vapour studied consisted entirely of monatomic carbon. This was based on spectroscopic observations by Brewer, Gilles and Jenkins (14) that there was less than 1% C_2 present in graphite vapour at 3500°K. The work of Honig and Chupka and Inghram has shown that this is not so, and Goldfinger (16) has demonstrated that his earlier observations are compatible with L_c = 170K.Cal if the presence of polyatomic carbon is taken into acc-:ount.

Further work by Chupka and Inghram (17) in which a Knudsen cell is coupled to a mass spectrometer has enabled the absolute pressures of the species C, C_2, C_3 to be measured in the effusing vapour. The method involves comparison of the intensities of the C^+, C_2^+ and C_3^+ ions with that of Ag^+ since the vapour pressure of silver at

the required temperatures is known. The results pointed unequivocally to L_c = 170K.Cal. /Mole. More recently, Thorn and Winslow (18) have produced further evidence in favour of L_c = 170K.Cal.

From the foregoing it may be seen that experimental evidence now entirely favours L_c = 170.K.Cal. Indirect methods on the other hand, until very recently, presented an even more confused picture.

(b) Indirect Methods:

The heat of formation of carbon monoxide is well known, as is the dissociation energy of oxygen [denoted by $D(O_2)$]. Thus the following thermochemical cycle may be constructed:

$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$	$\Delta H_f(CO)$
$C(s) \longrightarrow C(g)$	L_c
$\frac{1}{2}O_2(g) \longrightarrow O(g)$	$\frac{1}{2}D(O_2)$
$C(g) + O(g) \longrightarrow CO(g)$	$-D(C-O)$

where $\Delta H_f(CO)$ is the heat of formation of carbon monoxide from graphite at 298°K. hence a knowledge of the heat of dissociation of carbon monoxide [denoted D(C-O)] allows us to calculate L_c. A similar cycle can be em-:ployed to relate the heat of atomization of methane (or some simple derivative of methane) with known thermo-:chemical data to yield a value for L_c. e.g. consider CX_4 where X is equivalent to H, Cl, Br, F, or some com-:bination of these then

$$C(s) + 2X_2(g) \longrightarrow CX_4 \qquad \Delta H_f(CX_4)$$

$$C(s) \longrightarrow C(g) \qquad L_c$$

$$2X_2(g) \longrightarrow 4X(g) \qquad 2D(X_2)$$

$$C(g) + 4X(g) \longrightarrow CX_4 \qquad \Sigma D_4(CX_4)$$

where $\Delta H_f(CX_4)$ is the heat of formation of CX_4 and $D(X_2)$, the dissociation energy of X_2. We denote the heat of atomization of CX_4 by $\Sigma D_4(CX_4)$. The significance of this notation will be explained later.

1. Carbon Monoxide.

The spectrum of carbon monoxide is well known but its analysis depends on the interpretation of what were thought to be predissociations - a task which has proved exceedingly difficult and caused much controversy. The results are compatible with four distinct values of D(C-O) viz. 11.11, 9.65, 9.61, 9.14 eV leading to L_c = 170.4, 141.3, 135.8 and 125.0 K.Cal./ Mole respectively. Gaydon (2) and Herzberg (3) have critically reviewed this problem but have come to different conclusions, Gaydon preferring the highest value while Herzberg favours the lowest.

More recently, a close examination of the present evidence, coupled with the results of his own measurements has enabled Douglas (19) to pronounce in favour of D(C-O) = 11.11 eV. Barrow, on the other hand, has produced evidence of missing bands in the $b^3\Sigma^+ - a^3\Pi$ system which he

and his co-workers (20) consider points to an upper limit of 10.94 eV for D(C-O). A recent study of the absorption spectrum of carbon monoxide in the Vacuum Ultra Violet region (111) has shown that what were previously thought to be pre-dissociations are merely perturbation effects. They consider that their results are in keeping with D(C-O) = 11.11 eV. Further research is required to clear up these conflicting results.

Until quite recently, Hagstrum's (21) studies on the decomposition of carbon monoxide under electron impact were thought to provide strong evidence in favour of D(C-O) = 9.61 eV. In a careful study of the positive and negative ions produced in the mass spectrometer, the appearance potentials listed in table 1 were obtained. Also in this table are given the alternative dissociative mechanisms proposed by Hagstrum, together with the corresponding values of D(C-O). These values were calculated on the assumption that I(C) = 11.26 eV (which is well known form spectroscopy (22)) and the electron affinity of oxygen, EA(O) = 2.33 eV (23), the value which was preferred at the time. Lozier's Retarding Potential Method (24) was used to detect whether or not any of the ions were produced with Kinetic energy. In the cases studied, it was found that little or no kinetic energy was associated with the ionization processes.

TABLE 1.

D(C-O) as calculated from Appearance Potentials of Hagstrum (21).

	$A(R^+)$ eV.	Mechanism.	D(C-O) eV.
(1)	20.9	$C^+(^2P) + O^-(^2P)$	11.97
(1a)	"	$C^+(^2P) + O^{-*}$	9.64
(2)	22.8	$C^+(^2P) + O(^3P)$	11.54
(2a)	"	$C^+(^2P) + O(^1D)$	9.16
(3)	23.2	$C\ (^3P) + O^+(^4S)$	9.59
(4)	9.6	$C\ (^3P) + O^-(^2P)$	11.93
(4a)	"	$C\ (^3P) + O^{-*}$	9.6

O^{-*} denotes an O^- ion containing about 1.5 eV. excess vibrational or electronic energy.

If it is assumed that the fragments are produced solely in their electronic ground states only (1,2,3,4 above) then it is obvious that the electron impact results cannot distinguish between the possible values of D(C-O). Hagstrum considered then that since mechanisms 1,2, & 4 gave values of D(C-O) appreciably higher than the highest spectroscopically permitted value, the species produced in these reactions must be in excited electronic configurations. These alternative products are given in 1a,2a & 4a above together with the corresponding estimates of D(C-O). It will be observed that the upper limit of D(C-O) is now 9.64 eV. which excluded the two high values

and seemed to verify Herzberg's interpretation of the carbon monoxide spectrum.

Recent work, however, has caused Hagstrum to modify his previous arguments (26). The electron affinity of oxygen has been redetermined and a figure of 1.48 eV is now favoured (25). This means that D(C-O) as calculated from (1) and (4) above is reduced to about 11,12 and 11.08 eV respectively. Also Chupka and Inghram reported the detection of C^- ions in very low relative abundances with an appearance potential of about 23.2 eV. Thus assuming EA(C) = 2eV., D(C-O) = 11.6 eV. Hence we are entitled to say that Hagstrum's results do not exclude the possibility D(C-O) = 11.11 eV. Lagergren (27) has also obtained this value on the basis of electron impact studies on carbon monoxide.

The ion impact experiments of Lindholm (28) may be conveniently mentioned here. His method involved the bombardment of carbon monoxide with various ionic species (eg. He^+, A^+, Ne^+, N^+ etc.). These bombarding ions were generated from suitable substances in an ion source, accelerated and mass analysed by means of a magnet then passed into a collision chamber containing the gas under study. The product ions, in this case C^+ and O^+, were then accelerated, magnetically analysed, collected in the usual way and recorded. In effect the apparatus is a double mass spectrometer. When a bombarding ion enters the

collision chamber it is first of all thought to abstract an electron from a molecule of the gas to give a molecule ion which then decomposes in the normal way to give positive ions and neutral fragments e.g.

$$R^+ + CO \longrightarrow C^+O + R$$

$$CO^+ \longrightarrow C^+ + O$$

This sort of mechanism is preferred since the relative intensity of C^+ ions, say, depends on the electron affinity of the bombarding ion, (in this case, we mean by $EA(R^+)$ the energy given out by the reaction $R^+ + e^- \longrightarrow R$.) If $EA(R^+)$ is equal to the energy of production of C^+, then the abundance of C^+ will be a maximum, but if the production energy exceeds $EA(R^+)$ then the intensity of C^+ falls off rapidly. (The relative intensity of an ion R^+ will be denoted by $[R^+]$). The results showed that for bombardment with Ne^+, $[C^+]$ was fairly large and tended to increase with decrease in bombardment energy. This indicated that the energy of formation of the C^+ ion, denoted by $\mathcal{A}(C^+)$, is slightly smaller than $EA(Ne^+) = 21.56$ eV. Lindholm then suggested that $\mathcal{A}(C^+) = 20.9$ eV. corresponding to the electron impact $A(C^+)$ of the same value. However $\mathcal{A}(C^+)$ could not be interpreted by 1 or 1a above (table 1) since CO has insufficient electrons to give C^+ and O^- ions and at the same time neutralize Ne^+. Hence the decomposition process was considered to be

$$CO^+ \longrightarrow C^+(^2P) + O(^3P)$$

leading to D(C-O) = 9.61 eV.

2. Methane and its derivatives

Appearance potential studies of the ions C^+ and CH^+ derived from molecules of the type CH_3X have been carried out for X ≡ H, Cl, Br, I, CN and NO_2. If we consider the thermochemical cycle (1)

$C(s) + 1\frac{1}{2}H_2(g) + \frac{1}{2}X_2(g) \rightarrow CH_3X(g)$	$\Delta H_f(CH_3X)$
$C(s) \longrightarrow C(g)$	L_c
$1\frac{1}{2}H_2(g) \longrightarrow 3H(g)$	$1\frac{1}{2}D(H_2)$
$\frac{1}{2}X_2(g) \longrightarrow X(g)$	$\frac{1}{2}D(X_2)$
$C(g) + 3H(g) + X(g) \longrightarrow CH_3X(g)$	$-\Sigma D_4(CH_3X)$

we find that L_c is related to the heat of atomization of CH_3X by the equation :

$$L_c = \Sigma D_4(CH_3X) - \Delta H_f(CH_3X) - 1\tfrac{1}{2}D(H_2) - \tfrac{1}{2}D(X_2) \qquad (1.1)$$

The heats of formation of CH_3X are usually well known as are $D(H_2)$ and $D(X_2)$, hence L_c will depend upon a know-ledge of $\Sigma D_4(CH_3X)$. This quantity is defined to be the energy required to completely atomize CH_3X, i.e. the enthalpy change in the reaction:

$$CH_3X(g) \longrightarrow C(g) + 3H(g) + X(g)$$

whence $\Sigma D_4(CH_3X)$ is equal to the sum total of the energy required to break the four bonds of CH_3X in any order. E.g. assuming the most probable order of bond fission

$$\Sigma D_4(CH_3X) = D(CH_3\text{-}X) + D(CH_2\text{-}H) + D(CH\text{-}H) + D(C\text{-}H) \qquad (1.2)$$

Now if the C^+ ion, produced by electron impact, is acc-

:ompanied only by atomic species, then the appearance potent-:ial of C^+ is related to the heat of atomization by the equn.

$$A(C^+) = I(C) + \sum D_4(CH_3X) + E_k + E_e \qquad (1.3)$$

where I(C) is the ionization potential of carbon. E_k and E_e measure respectively the amount of kinetic and electronic excitational energy imparted to the fragments during electron impact. Similarly, if H_2 or HX is formed along with C^+ then

$$A(C^+) = I(C) + \sum D_4(CH_3X) - D\begin{Bmatrix}(H_2)\\(HX)\end{Bmatrix} + E_k + E_e \qquad (1.4)$$

where $D\begin{Bmatrix}(H_2)\\(HX)\end{Bmatrix}$ refers to H_2 or HX as the case may be. Hence a knowledge of $A(C^+)$ enables (assuming E_k and E_e to be zero) an upper limit for L_c to be obtained.

Methane and the methyl halides were studied by Branson and Smith (29). Their values of $A(C^+)$ together with those of L_c have been listed in Table 2. They considered the di-:ssociative mechanism to be of the form

$$CH_3X \longrightarrow C^+ + 3H + X$$

which resulted in $L_c \sim 140$ K.Cal. Assumption that H_2 or HX molecules were formed required that L_c = 220-240 K.Cal. which were considered to be improbably high.

TABLE 2.

L_c values calculated from $A(C^+)$ of Branson and Smith (29)

Compound	$A(C^+)$ eV.	L_c(K.Cal.)
CH_4	26.9±0.2	139±5
CH_3Cl	26.0±0.3	139±7
CH_3Br	25.4±0.4	140±10
CH_3I	24.4±0.4	136±10

CH_3CN was studied by McDowell and Warren (30). They obtained two values for $A(C^+)$ = 22.6 $\pm$0.2 eV. and 27.0 $\pm$0.3 eV. The difference, 4.4 eV., was taken to represent $D(H_2)$ and the appearance potentials were taken to refer to the mechanisms

$$CH_3CN \longrightarrow C^+ + H_2 + H + CN \qquad A(C^+) = 22.6 \text{ eV.}$$

$$CH_3CN \longrightarrow C^+ + 3H + CN \qquad A(C^+) = 27.0 \text{ eV.}$$

the corresponding values of L_c being 136 and 134 K.Cal./Mole respectively. These two workers (31) also measured the appearance potentials of CH_3^+, CH_2^+, CH^+ and C^+ from methane. These were combined with the appropriate ionization potentials to yield the bond dissociation energies $D(CH_3\text{-}H)$, $D(CH_2\text{-}H)$, $D(CH\text{-}H)$ and $D(C\text{-}H)$ which were then compared with the results of previous workers. From this, it was deduced that C^+ from methane was produced together with four hydrogen atoms whence L_c was estimated to be $\sim$130 K.Cal/Mole.

McDowell and Warren's experiments on methane were repeated by Langer, Hipple and Stevenson (32) who, in addition, measured $A(C^+)$ from the CH_3 and CH_2 radicals. In Table 3 are given the three values of $A(C^+)$ together with the presumed dissociation mechanisms and the corresponding values of L_c.

TABLE 3.

L_c values calculated from $A(C^+)$ of Langer, Hipple & Stevenson

$A(C^+)$ eV.	Compound.	Dissoc. Mech.	L_c(K.Cal)
27.0$\pm$0.2	CH_4	$C^+ + 4H$	137
17.8$\pm$0.2	CH_3	$C^+ + H_2 + H$	130

Table Cont'd/

TABLE 3 (Cont'd).

$A(C^+)$ eV.	Compound	Dissoc. Mech.	L_o(K.Cal.)
18.0±0.2	CH_2	$C^+ + 2H$	110

The fragmentation processes chosen were the simplest consistent with the values of L_c which were spectroscopically permitted, and thus seem to point unequivocally to a low value of L_c.

Brackett (33), however, has recently pointed out that the above results can be interpreted in terms of L_c = 170 K. Cal. if it is assumed that instead of two neutral hydrogen atoms, two negatively charged H^- ions are formed. Since EA(H) = 0.74 eV., this proposal requires 34 K.Cal. to be added to the estimated values of L_c. In Table 4, L_c has been calculated on this basis for the compounds discussed above.

TABLE 4.

Compound	$A(C^+)$ eV.	Dissoc. Mech.	L_o(K.Cal.)
CH_4	26.7(av.)	$C^+ + 2H + 2H^-$	164
CH_3Cl	26.0±0.3	$C^+ + 2H + H + Cl$	171
CH_3Br	25.4±0.4	$C^+ + 2H + H + Br$	174
CH_3I	24.9±0.3	$C^+ + 2H + H + I$	170
CH_3CN	27.0±0.3	$C^+ + 2H + H + CN$	168
CH_3	17.8±0.2	$C^+ + 2H + H$	147
CH_2	18.0±0.2	$C^+ + 2H$	144

In addition, Morrison and Stanton (69) have shown that both C^+ and CH^+ derived from methane possess significant amounts of kinetic energy. They have attempted on this basis to re-

:concile the results of McDowell and Warren (31) with L_c = 170K.Cal.

The evidence from the appearance potentials of CH^+ is equally indecisive. $A(CH^+)$ is related to $\sum D_4(CH_3X)$ by the equation

$$A(CH^+) = I(CH) + \sum D_4(CH_3X) - D(C-H) + E_k + E_e \quad (1.5)$$

if only atomic species accompany CH^+ and

$$A(CH^+) = I(CH) + \sum D_4(CH_3X) - D(C-H) - D\binom{H_2}{HX} + E_k + E_e \quad (1.6)$$

if H_2 or HX are formed. Of the several possible modes of decomposition we shall consider only those two, (a) and (b), which yield values of L_c reasonably close to the spectroscopically allowed ones.

$$CH_3X \longrightarrow CH^+(X.^1\Sigma^+) + 2H + X \quad (a)$$

$$CH_3X \longrightarrow CH^+(A.^1\Pi) + H_2 + X \quad (b)$$

Process (a) coresponds to equation (1.5) ($E_k = E_e = 0$) while (b) requires the use of (1.6) with E_e = 2.99 eV. which is the energy separation of the $X.^1\Sigma^+$ and $A.^1\Pi$ electronic states. D(C-H) = 3.47 eV. is well known from spectroscopic measurements (32). The values of $A(CH^+)$ obtained for methane and the methyl halides together with the corresponding values of L_c calculated by both (1.5) and (1.6) are given in Table 5

TABLE 5.

L_c values calculated from $A(CH^+)$

Compound	$A(CH^+)$ eV.	L_c(K.Cal.) Calc. by (1.5)	L_c(K.Cal.) Calc. by (1.6)	Ref.
CH_4	23.0(av.)	125	160	(4b)
CH_3Cl	22.4±0.2	134	169	(29)
CH_3Br	21.8±0.4	134	169	(29)
CH_3I	21.2±0.5	136	171	(29)

Hence, depending on the process selected, the results can be interpreted in terms of either the high or the low value of L_c.

The appearance potentials of CH_3^+, CH_2^+ and CH^+ from CH_3NO_2 have been measured by Kandel (35). His results show that if $D(CH_2\text{-}H)$ = 3.45 eV. and $D(CH\text{-}H)$ = 3.40 eV. as obtain-:ed by McDowell and Warren (31), then $D(CH_3\text{-}NO_2)$ = 2.55 eV. in good agreement with thermochemical measurements (5c), thus confirming McDowell and Warren's experiments. This naturally leads to L_c = 130 K.Cal. since the other thermochemical data is beyond dispute. There is, however, some uncertainty as to the structure of the NO_2 fragment produced during the de-:composition of Nitro-methane. If this radical undergoes rearrangement then Kandel's conclusions may require to be modified.

From the foregoing, it will be evident that no value of L_c can be taken as unequivocally established. Although the

weight of evidence, especially from the vapour pressure measurements and the electron impact data on carbon-monoxide, comes down on the side of a high value, anomalies such as the work of Lindholm and Kandel require further thought before L_c = 170 K.Cal. can be finally accepted.

The Heat of Dissociation of Nitrogen.

The studies leading to the determination of the heat of dissociation of nitrogen, denoted $D(N_2)$, parallel closely those performed to evaluate D(C-O) both in the methods used and in the difficulties encountered. Various authors have at different times proposed widely differing values for $D(N_2)$ (See Gaydon (2b) for full list and references) but it has now become evident that only two need be seriously considered. These are the values 7.373 eV and 9.756 eV. put forward respectively by Herzberg (3b) and Gaydon (2b), on the basis of different interpretations of predissociations in the nitrogen spectrum. More recent spectroscopic studies have added much evidence and Douglas (19) has pointed out that most of the available spectroscopic data can be readily interpretated in terms of $D(N_2)$ = 9.756 eV, but no direct proof of the exact value of $D(N_2)$ has yet been provided.

Several thermal methods (36-40) have been applied from time to time. They all provide results which exclude the low value of $D(N_2)$, but suffer from the defect that they

require relatively large amounts of ancillary information which adds considerably to the possibility of experimental error.

Electron impact experiments have, until quite recently, proved equally inconclusive. Hagstrum (21) showed that in the electron impact induced breakdown of nitrogen, only positively charged atomic nitrogen and neutral nitrogen atoms were formed. No trace of N^- ions were detected, and in addition the N^+ ions were formed with practically no excess kinetic energy - an observation which was later confirmed by Thorburn and Craggs (41). From his appearance potential measurements, Hagstrum concluded that the dissociation products were

$$N_2(^1\Sigma_g^+) \xrightarrow{e} N^+(^3P) + N(^2D) + 2e^-$$

and that $D(N_2) = 7.37$ eV. However, new electron impact studies, employing nearly mono-energetic electrons, have shown these deductions to be incorrct. Clarke (42) using a velocity selector, obtained $A(N^+) = 24.35 \pm 0.1$ eV. with higher breaks at 2.36 eV. above the first and at 1.4 eV above the second. The difference between the ^2D and ^2P levels are separated by 1.191 eV. Hence it was assumed that Clarke's results referred to dissociation mechanisms in which N^+ ions were produced in their ground state and N atoms in their successive excited states, from which it was deduced that $D(N_2) = 9.756$ eV.

Clarke's observations were confirmed in detail by Frost and McDowell who employed a pulse technique to obtain mono-:energetic electrons. The Retarding Potential Difference method of Fox (44) has been employed by Burns (45), with somewhat different results. In addition to the three breaks in the ionization efficiency curve of N^+ observed by Clarke, Burns noted a fourth discontinuity lying at about 1.9 eV. above the lowest break. Since the ^1D state of N^+ lies at 1.90 eV. above the ground ^3P state the dissociative process was considered to be

$$N_2(^1\Sigma_g^+) \longrightarrow N^+(^1D) + N(^4S)$$

which gave rise to $D(N_2) = 9.8$ eV. This extra dissociat-:ion mechanism was not observed by Frost and McDowell, but this may be due to Burns using a more homogenious electron beam in his ion source.

Thus the direct methods point, with only a little un-:certainty to $D(N_2) = 9.756$ eV.

Indirect Methods.

The indirect approach has been largely centered on the determination of the heat of dissociation of nitric oxide, denoted D(N-O), which is related to $D(N_2)$ by the cycle:

$NO \longrightarrow N(g) + O(g)$	$D(N\text{-}O)$
$\frac{1}{2}N_2(g) \longrightarrow N(g)$	$\frac{1}{2}D(N_2)$
$\frac{1}{2}O_2(g) \longrightarrow O(g)$	$\frac{1}{2}D(O_2)$
$NO \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$	$-\Delta H_f(NO)$

Spectroscopic observations on nitric oxide lead once again to conflicting results, (2c) but the most recent measurements (46) - (48) now favour D(N-O) = 6.48 eV. corresponding to $D(N_2)$ = 9.756 eV.

The strongest evidence in favour of the low value of $D(N_2)$ was the electron impact experiments carried out by Hagstrum (21) on nitric oxide. Combination of his results with EA(O) = 2.33 eV. (as was then thought) produced the unequivocal value of 5.29 eV. for D(N-O) leading to $D(N_2)$ = 7.37 eV. However, in light of the most recent EA(O) = 1.48 eV., (25) Hagstrum's results can now be interpreted in terms of either the high or the low value of D(N-O). The appearance potential of the various ions are given in table 6 together with the appropriate dissociation states and the corresponding values of D(N-O).

TABLE 6

Values of D(N-O) from measurements of Hagstrum (21) (taking EA(O) = 1.48 eV.

A.P. eV.	Products	D(NO)	Products	D(NO)
21.7	$N^+(^1D) + O(^3P)$	5.3	$N^+(^3P) + O(^3P)$	7.2
19.9	$N^+(^1D) + O^-(^2P)$	5.0	$N+(^3P) + O^-(^2P)$	6.9
5.3	$N(^4S) + O^{-*}$	5.3	$N(^4S) + O^-(^2P)$	6.8
3.2	$N(^4S) + O^-(^2P)$	4.7		
20.6	$N(^2D) + O^+(^4S)$	4.6	$N(^4S) + O^+(^4S)$	7.0

It will be seen that with one exception, the measured app-

:earance potentials can give rise to either value of D(N-O) and hence $D(N_2)$ depending on the assumptions made as to the electronic states of the fragments.

In the same way as $A(C^+)$ from methane was used to est-:imate a value for L_c, the appearance potential of nitrogen ions derived from the electron impact of ammonia may be em-:ployed to find $D(N_2)$. $A(N^+)$ is related to $D(N_2)$ by the cycle:

$NH_3 \longrightarrow N(g) + 3H(g)$	$\Sigma D_3(NH_3)$
$\frac{1}{2}N_2(g) \longrightarrow N(g)$	$\frac{1}{2}D(N_2)$
$1\frac{1}{2}H_2(g) \longrightarrow 3H(g)$	$1\frac{1}{2}D(H_2)$
$NH_3(g) \longrightarrow \frac{1}{2}N_2(g) + 1\frac{1}{2}H_2(g)$	$-\Delta H_f(NH_3)$

whence $D(N_2) = 2\Sigma D_3(NH_3) - 3D(H_2) + 2\Delta H_f(NH_3)$ (1.7)

where $\Sigma D_3(NH_3)$ is the heat of atomization of ammonia and the other symbols have their usual significance.

Two values for $A(N^+)$ from NH_3 have been reported by Mann, Hustrulid and Tate (49) - 25.0±0.5 eV. and 28.1±0.7 eV. In Table 7 a dissociative mechanism has been pro-:posed which, on combination with the appropriate appearance potential, gives $D(N_2) \simeq 9$ eV.

TABLE 7

$D(N_2)$ calculated from electron studies on NH_3(Mann et.al.)

$A(N^+)$ eV.	Process.	$D(N_2)$ eV.
25.0±0.5	$N^+(^3P) + H + 2H^-$	9.6
28.1±0.7	$N^+(^1D) + 3H$	9.0

No similar dissociative states can be chosen to make $D(N_2)$ = 7.4 eV. Other fragmentation routes which might selected give values of $D(N_2)$ which are either improbably high, or appreciably lower than 7.4 eV. However, owing to the re-:latively large experimental error associated with these ob-:servations, it is obvious that they can only provide an indication of $D(N_2)$ = 9.756 eV. not incontrovertible proof.

The [illegible] in this work were those of the CX_2 and CX radical For this purpose, a [illegible] was designed to [illegible] the appropriate free radical whose adiabatic potential could then be measured in the usual way. Since [illegible] was one purely of ionization, the appea potential of CX_2^+ is equal to the vertical ioniza potential of the corresponding radical. The ioniz potentials of CF_2 and CCl_2 radicals were obtained

EXPERIMENTAL.

(a) The Latent Heat of Sublimation of Carbon.

In view of the foregoing, it was decided to conduct an electron impact study on the compounds CCl_4, CF_4 and CBr_4 along these lines of McDowell and Warren (31) in their experiments on methane. The data required consisted of the appearance potentials of the CX_3^+, CX_2^+, CX^+ and C^+ ions (X≡F, Cl, Br) from CX_4. Such appearance potentials had already been obtained for CCl_4 by Baker and Tate (50) and for CF_4 and CCl_4 by Warren and Craggs (51). However, certain ionisation potentials were unknown, and no definite conclusions as to the fragmentation process could be made and hence no estimation of L_c was given.

The ionization potentials requiring to be measured in this work were those of the CX_2 and CX radicals. For this purpose, a technique was developed to generate the appropriate free radical whose appearance potential could then be measured in the usual way. Since the mechanism was one purely of ionization, the appearance potential of CX_r^+ is equal to the vertical ionization potential of the corresponding radical. The ionization potentials of CF_3 and CCl_3 radicals were obtained by Farmer and his co-workers (52) and their values were used in this work.

The reasons for the selection of those compounds for

study were:

(1) All could be obtained in a state of high purity.

(2) The neutral X or X_2 fragments produced during the Electron induced dissociation of CX_4 are heavy in comparison with the accompanying C^+, hence any kinetic energy associated with the process would be imparted preferentially to the C^+. Methods are available (21) for the detection of kinetic energy ($\geq$ 0.1 eV) if possessed by an ion, but there is no way of indicating translational energy in a neutral radical. (see further below)

From the appearance and ionization potential, and data obtained, it was hoped that a common dissociative mechanism might be postulated for all three compounds, whence an unequivocal value for L_c might be deduced.

1. Apparatus and Method

The measurements were made with a Metropolitan-Vickers model M.S.2 mass spectrometer with modifications described by Reed (53). For the generation of free radicals and all experiments on CBr_4, the convential gas handling system was replaced by one designed by ourselves. This took the form of a bulb containing sample under study. Attached to the bulb was a micrometer needle valve backed by a sintered disc, which served to reduce the vapour pressure of the sample to about 10^{-5}mm. The gas at low pressure then entered a pyrolisis chamber which contained

an electrically heated tungsten filament whose temperature could be controlled by a manually operated resistance. The gases, after impinging on the hot wire, were then led along a short rectilinear path into the ionization head, the terminal sinter having been removed for this purpose.

The procedure was then as follows. The mas spectro-:meter was adjusted to collect ions of the chosen mass. The sample gas was then allowed to enter the ion source and the graph of ion current against electron accelerating voltage constructed in the normal way. A sample of argon was then admitted at a pressure such that the ion current of A^+ at say 25 volts (50 volts in the case of C^+) was nearly equal to that of the ion under investigation at the same voltage. The ionization efficiency curve of A^+ was then measured and the appearance potential of the required ion obtained by Warren's method (54), (taking I (A) = 15. 816 eV.)

The ionization potential was then measured by setting the electron accelerating voltage to about 12 volts or some suitable value somewhat greater than the presumed ion-:ization potential. The sample vapour was then admitted to the combustion chamber, the tungsten wire heated and the temperature adjusted until the measured number of particles was a maximum. The chamber was maintained at this temper-:ature while the ion current-ionizing voltage graph was ploted as before.

With this technique, it was unsuitable to use argon as a calibration gas. Instead, since the ionization potentials of water and carbon monoxide are accurately known and since they are always present in the background spectrum of the machine to some extent, these two gases were imployed as internal standards. ($I(H_2O)$ = 12.16 eV.; $I(CO)$ = 14.009 eV.) (4c).

The pyrolisis of CF_4 did not yield the radicals CF_2 and CF in satisfactory yields. They were obtained, however, in relatively high concentration by thermal decomposition of CF_2Cl_2 and $CFCl_3$ respectively. In the case of CCl_4 and CBr_4 the CX_2 and CX radicals could be produced by "cracking" CX_4 (X = Cl,Br).

2. Materials.

The halo-carbon materials were all of A.R. grade or equivalent while the argon was of spectroscopic purity. No further purification was attempted since mass spectral investigation showed no significant amounts of impurity present.

RESULTS.

The results of the investigations are shown in Tables 8a and 8b. The uncertainties attached to the figures are standard deviations. Literature values are entered in Table 8c for comparison.

TABLE 8a

Appearance potentials of positive ions from CF_4, CCl_4, CBr_4(eV.)

Species.	X = F	X = Cl	X = Br
CX_3^+	15.40±0.05	11.90±0.05	9.95±0.05
CX_2^+	22.27±0.05	16.10±0.05	12.32±0.05
	23.9 ±0.1	18.6 ±0.1	14.3 ±0.1
CX^+	27.32±0.05	19.35±0.05	16.37±0.05
	28.6 ±0.1	21.9 ±0.1	18.3 ±0.1
C^+	27.92±0.05	19.54±0.05	18.9 ±0.1
	29.47±0.05	22.05±0.05	20.77±0.05
	30.9 ±0.1	24.5 ±0.1	22.8 ±0.1

TABLE 8b

Ionization potentials of halocarbon radicals from CX_4 eV.

Species.	X = F	X = Cl	X = Br
CX_3	10.15±0.05	-	-
CX_2	13.3 ±0.1	13.1 ±0.1	10.1 ±0.1
CX	13.8 ±0.1	12.9 ±0.1	10.4 ±0.1

TABLE 8c

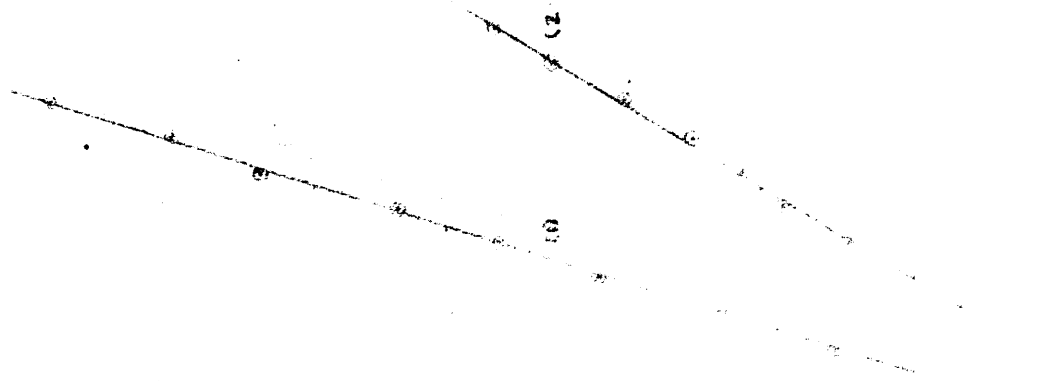
Literature values of appearance and ionization potentials for CX_4.

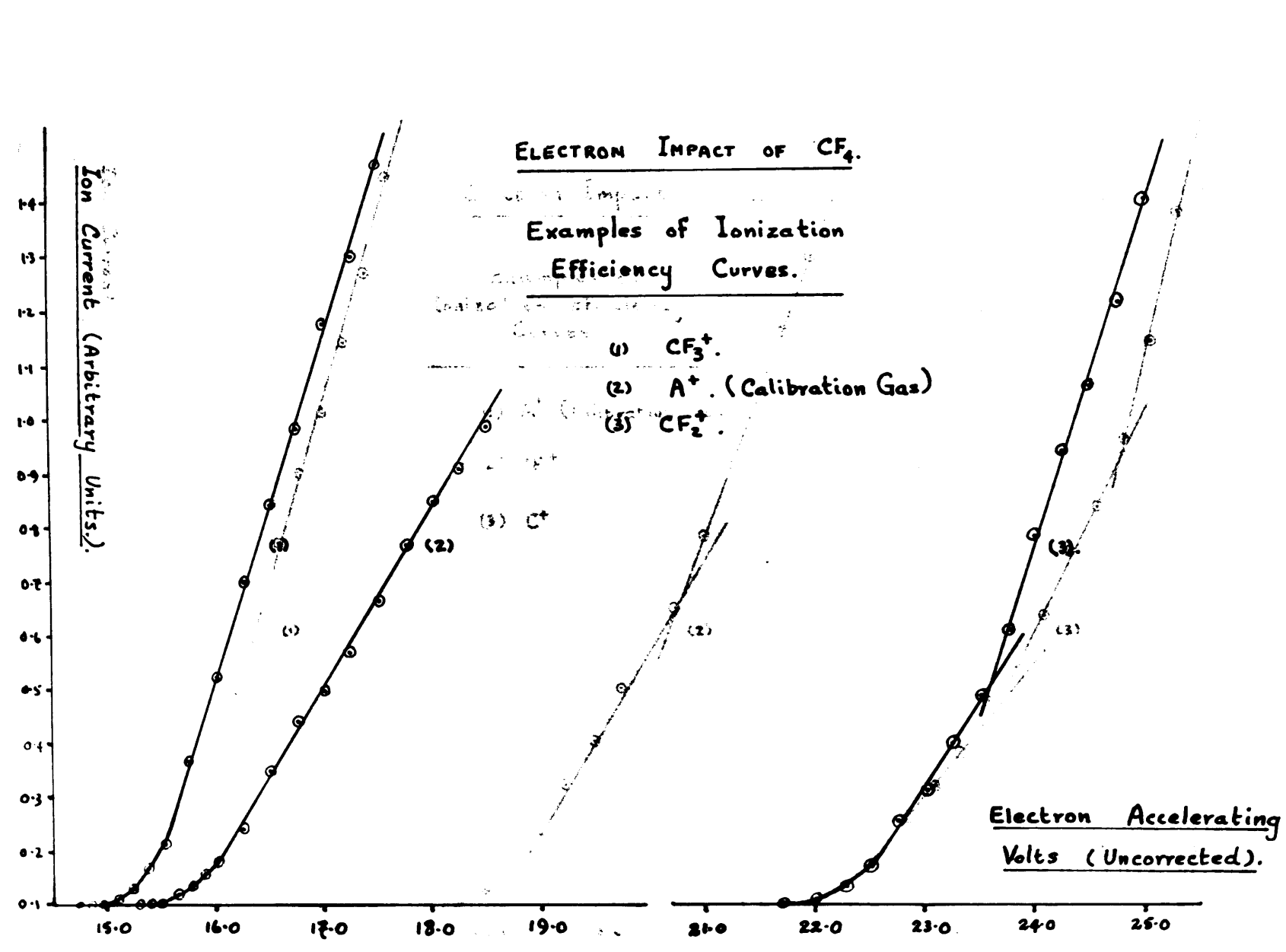
	Appearance Potentials eV.(51)		Ionization Potentials eV.		
Species	X ≡ F	X ≡ Cl	X ≡ F	X ≡ Cl (52)	
CX_3	15.44±0.05	11.83±0.05	10.10±0.05	8.78±0.05	(52)
CX_2	22.4 ±0.2	16.1 ±0.1	-	13.2 ±0.2	(55)
CX	27.2 ±0.5	19.3 ±0.2	-	-	

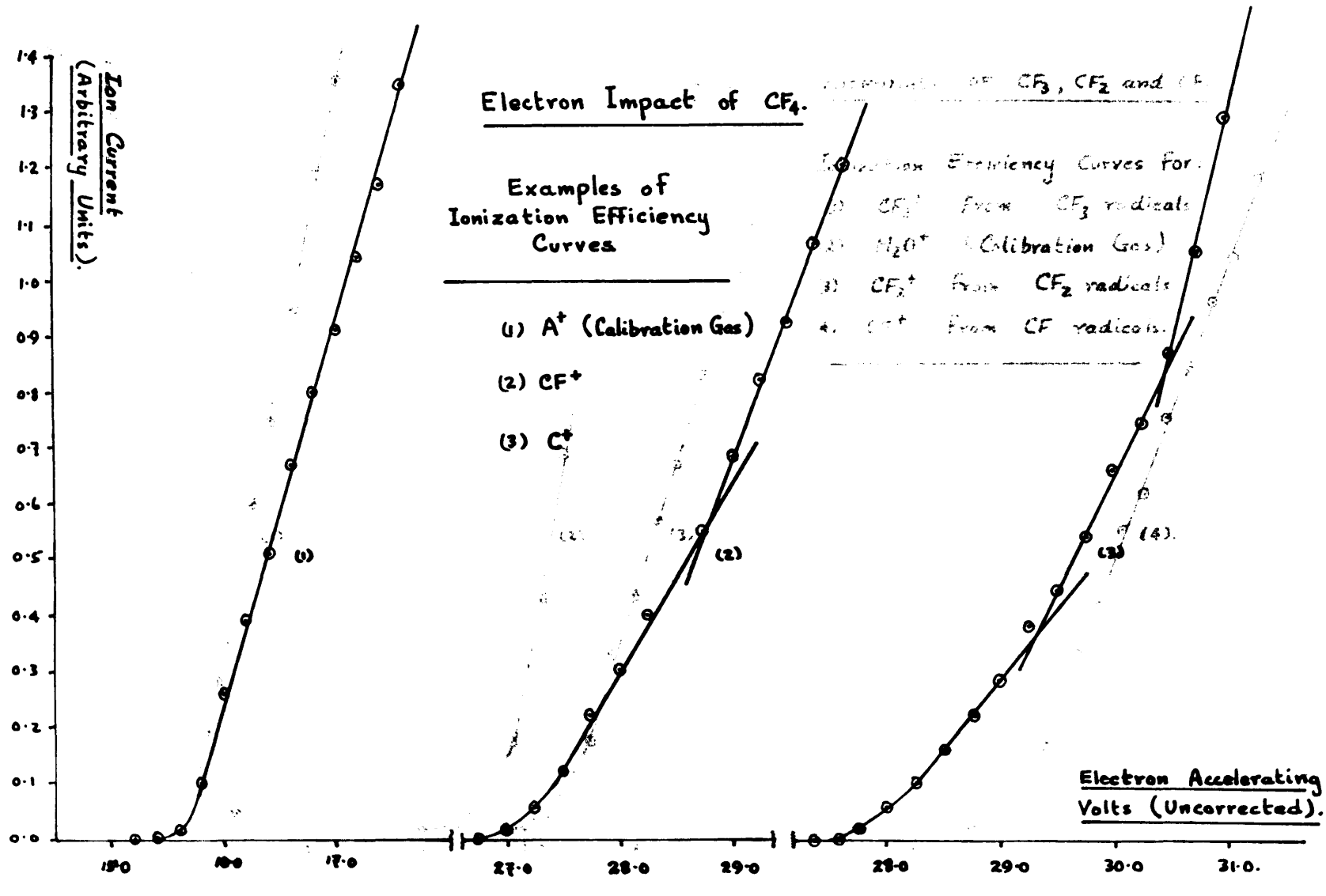
TABLE 9

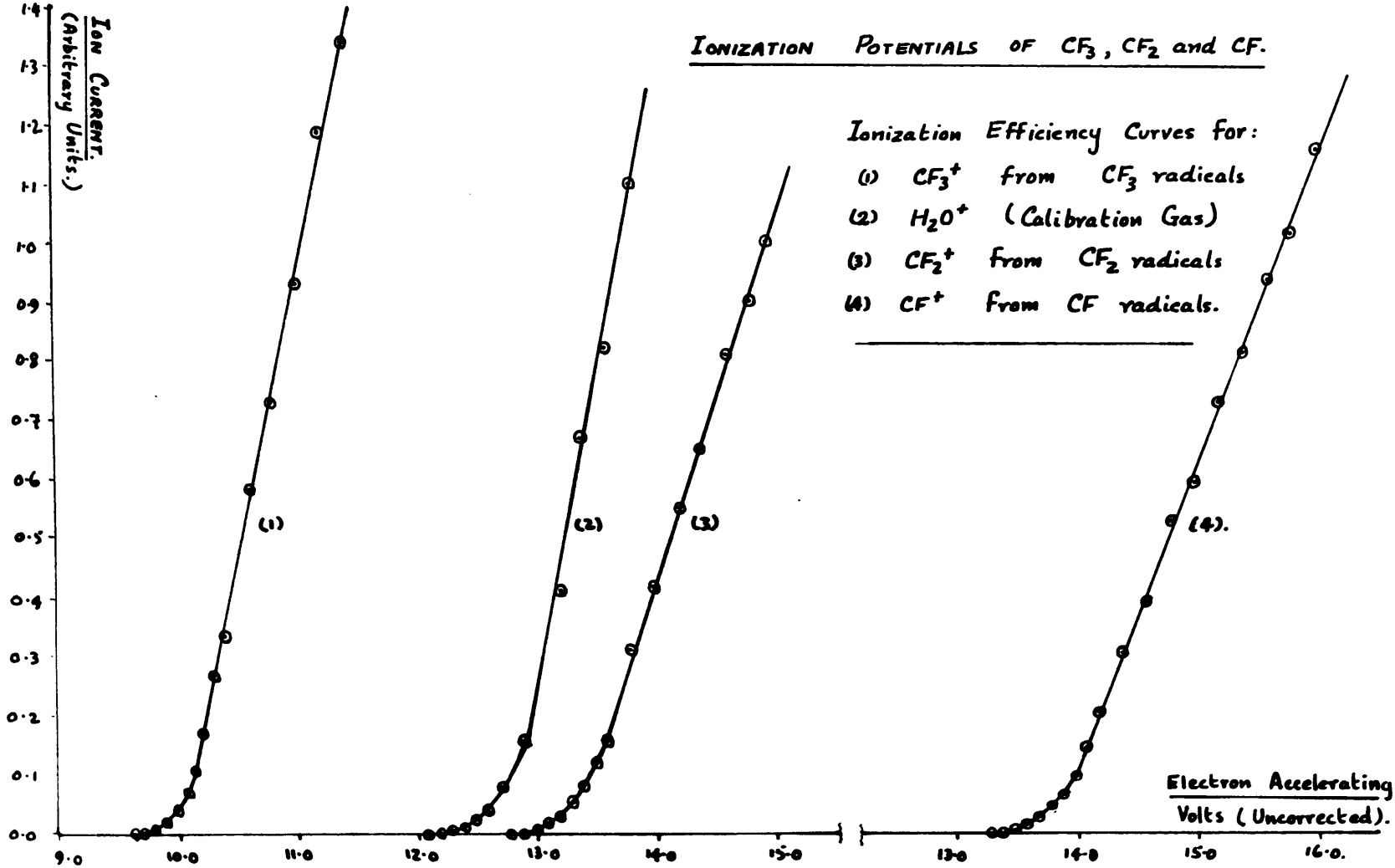
Mass spectrum of CBr_4 at various impact voltages.

Impact Voltage eV.	Relative intensity.			
	CBr_3^+	CBr_2^+	CBr^+	C^+
20	9.47	4.61	1.00	-
35	2.70	0.68	1.00	0.04
50	1.40	0.80	1.00	0.05




Electron Impact of CF_4.
Examples of Ionization Efficiency Curves.
(1) CF_3^+.
(2) A^+. (Calibration Gas)
(3) CF_2^+.
(4) C^+
Ion Current (Arbitrary Units).
Electron Accelerating Volts (Uncorrected).
15·0
16·0
17·0
18·0
19·0
21·0
22·0
23·0
24·0
25·0


Electron Impact of CF_4.
Examples of Ionization Efficiency Curves
(1) A^+ (Calibration Gas)
(2) CF^+
(3) C^+
Ion Current (Arbitrary Units).
Electron Accelerating Volts (Uncorrected).
(1)
(2)
(3)
(4)
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
19·0
18·0
17·0
27·0
28·0
29·0
28·0
29·0
30·0
31·0.


Ionization Potentials of CF_3, CF_2 and CF.
Ionization Efficiency Curves for:
(1) CF_3^+ from CF_3 radicals
(2) H_2O^+ (Calibration Gas)
(3) CF_2^+ from CF_2 radicals
(4) CF^+ from CF radicals.
Ion Current. (Arbitrary Units.)
Electron Accelerating Volts (Uncorrected).
(1)
(2)
(3)
(4).
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1·1
1·2
1·3
1·4
9·0
10·0
11·0
12·0
13·0
14·0
15·0
13·0
14·0
15·0
16·0.

DISCUSSION.

In an electron impact induced dissociation of a molecule $R_x - R_y$ of the type

$$e^- + R_x - R_y \longrightarrow R_x^+ + R_y + 2e^-$$

the appearance potential of R_x^+, denoted $A(R_x^+)$, is related to the heat of dissociation $D(R_x - R_y)$ by the equation:

$$A(R_x^+) = I(R_x) + D(R_x - R_y) + E_k + E_e$$

where $I(R_x)$ is the ionization potential of R_x, while E_k and E_e measure respectively the amount of kinetic and electronic excitational energy imparted to the fragments during decomposition. Measurements of the half beam widths of the ions C^+ from CCl_4 and CBr_4 were carried out (31). No significant broadening was observed compared with ions H_2O^+, CO^+ or O_2^+. These C^+ ions are regarded as representing favourable cases for the detection of kinetic energy and since none was observed, it is concluded that little or no kinetic energy is associated with any of the dissociative processes given below.

It is also considered that the products of ionization are formed in their electronic ground state. Higher "breaks" were observed in the ionization efficiency curves for CX_2^+ and CX^+ but since the nature of the excited states of these ions is unknown, no attempt was made to discuss them. Hence in the above equation, it is assumed that $E_k = E_e = 0$.

Note: In all occasions where a series of appearance pot-:entials are observed for a particular ion, they will be referred to as $A_1(R^+)$, $A_2(R^+)$, - - - $A_n(R^+)$ in ascending order of energy.

Dissociation Processes

1. $\underline{CX_3^+}$: The initial dissociation namely

$$e^- + CX_4 \longrightarrow CX_3^+ + X + 2e^- \qquad (a)$$

has already been considered for CCl_4 by Farmer et.al. (52) who have rejected the alternative mechanism (b)

$$e^- + CX_4 \longrightarrow CX_3^+ + X^- + e^- \qquad (b)$$

Hence we have

$$A(CX_3^+) = I(CX_3) + D(CX_3\text{-}X)$$

$D(CCl_3\text{-}Cl)$ is found to be 3.12±0.1 eV. in good agreement with Farmer's value of 2.95±0.15 eV. It will be noted that $I(CF_3)$ = 10.15±0.05 eV. is also in good agreement with that already reported (52) and $D(CF_3\text{-}F)$ = 5.25±0.1 eV. agrees well with that obtained by Farmer namely 5.33±0.11 eV. If mechanism (b) is assumed to calculate $D(CF_3\text{-}F)$ the result is increased by the electron affinity of fluor-:ine to $D(CF_3\text{-}F)$ = 9.2 eV. which is much too high.

CBr_3 radicals could not be generated in sufficient yield to measure $I(CBr_3)$, but Szwarc and Sehone (56) have measured $D(CBr_3\text{-}Br)$ = 2.16±0.05 eV. Combination of this with the measured $A(CBr_3^+)$ gives $I(CBr_3)$ = 8.04±0.1 eV. according to (a) and 11.4 eV. by (b). From a considerat-

:ion of the sizes and polarizabilities of the substituents on the carbon, we would expect the ionization potential should be progressively lowered in the series CF_3, CCl_3 and CBr_3. Taking $I(CBr_3)$ = 8.04 eV; this is shown to be the case. Assumption of $I(CBr_3)$ = 11.4 eV. infers that $I(CBr_3)$ $>I(CF_3)$ which is most unlikely since fluorine has a higher electron affinity than bromine. By similar arguments, all dissociative mechanisms which involve negatively charged halogens ions are rejected.

2. $\underline{CX_2^+}$: This ion can arise by either of the routes (c) or (d)

$$e^- + CX_4 \longrightarrow CX_2^+ + X_2 + 2e^- \qquad (c)$$

$$e^- + CX_4 \longrightarrow CX_2^+ + 2X + 2e^- \qquad (d)$$

It will be seen from table 8a that two values of $A(CX_2^+)$ were observed. The differences between $A_1(CX_2^+)$ and $A_2(CX_2^+)$ for X≡F, Cl and Br are respectively 1.63 eV; 2.50 eV. and 1.98 eV. These differences are close to the respective values of $D(X_2)$; thus it is cosidered that $A_1(CX_2^+)$ refers to (c) and $A_2(CX_2^+)$ to (d). From (c) and (d), equations (2.1) and (2.2) may be derived

$$(c) \sim A_1(CX_2^+) = I(CX_2) + \Sigma D_2(CX_4) - D(X_2) \qquad (2.1)$$

$$(d) \sim A_2(CX_2^+) = I(CX_2) + \Sigma D_2(CX_4) \qquad (2.2)$$

where $\Sigma D_2(CX_4) = D(CX_3\text{-}X) + D(CX_2\text{-}X)$ and $D(X_2)$ is the heat of dissociation of the appropriate halogen molecule. Substitution of the appearance and ionization potentials in the above equations gives the results quoted in table 10a.

TABLE 10a

	By Equn. (2.1)		By Equn. (2.2)	
X	$\Sigma D_2(CX_4)$ eV.	$D(CX_2-X)$ eV.	$\Sigma D_2(CX_4)$ eV.	$D(CX_2-X)$ eV.
F	10.53±0.15	5.28±0.25	10.6±0.2	5.35±0.3
Cl	5.48±0.15	2.36±0.25	5.5±0.2	2.4±0.3
Br	4.20±0.15	2.04±0.2	4.2±0.2	2.04±0.25

The present estimate of $D(CCl_2-Cl) = 2.36\pm0.25$ eV. is in good agreement with the value of 2.69±0.31 eV. reported by Blanchard and Le Goff (55). The choice of these reaction mechanisms is supported for CCl_4 by the consideration that the CCl_2 radical is now postulated as an intermediate in the formation of phenolic aldehydes by the Reimer - Tiemann reaction (57). Consequently it must be fairly readily formed and possess some stability. This suggests that the dissociation energy of the second bond in CCl_4 should not be much greater than the first, and that $D(CCl-Cl)$ be not less than $D(CCl_2-Cl)$. It will be shown below that this latter statement is in fact true.

Another verification of the choice of decomposition routes is that assignment of $A_1(CBr_2^+)$ to equation (2.2) would result in $D(CBr_2-Br) \simeq 0$. Thus the removal of one bromine atom from CBr_4 would be followed by the very ready loss of another and consequently an abscence of CBr_3^+ ions from the mass spectrum. However, as Table 9 clearly shows,

CBr_3^+ is the most abundant ion in the spectrum at the voltages given. Hence the present selection of dissociat-:ive processes is considered to be justified.

3. $\underline{CX}^+$: In this instance, we record two values for $A(CX^+)$. As before, the differences between each pair are in good agreement with the corresponding value of $D(X_2)$. Therefore, by analogy with the previous case, it is thought that the lower appearance potential $A_1(CX^+)$ refers to mech-:anism (e) and the higher, $A_2(CX^+)$, to (f).

$$e^- + CX_4 \longrightarrow CX^+ + X_2 + X + 2e^- \qquad (e)$$

$$e^- + CX_4 \longrightarrow CX^+ + 3X + 2e^- \qquad (f)$$

whence $(e) \sim A_1(CX^+) = I(CX) + \Sigma D_3(CX_4) - D(X_2)$ (2.3)

$$(f) \sim A_2(CX^+) = I(CX) + \Sigma D_3(CX_4) \qquad (2.4)$$

where $\Sigma D_3(CX_4) = D(CX_3\text{-}X) + D(CX_2\text{-}X) + D(CX\text{-}X)$

hence $D(CX\text{-}X) = \Sigma D_3(CX_4) - \Sigma D_2(CX_4)$

Substitution of the appropriate data gives the results listed in Table 10b

TABLE 10b

	By Equn. (2.3)		By Equn. (2.4)	
X	$\Sigma D_3(CX_4)$ eV.	D(CX-X) eV.	$\Sigma D_3(CX_4)$ eV.	D(CX-X) eV.
F	15.08±0.15	4.55±0.3	14.8±0.2	4.2±0.4
Cl	8.93±0.15	3.45±0.3	9.0±0.2	3.5±0.4
Br	7.95±0.15	3.65±0.3	7.9±0.2	3.7±0.4

It has been decided that mechanism (f) does not apply to $A_1(CX^+)$ since in this case, equation (2.4) would yield improbably low values for D(CCl-Cl) and D(CBr-Br) namely 1.0

and 1.76 eV. respectively.

4. C^+: Here, three well defined and reproducible "breaks" are observed in the ionization efficiency curve of C^+ from each CX_4. The energy differences, as in the previous two cases are approximately equal to the corresponding value of $D(X_2)$. Thus it is assumed that these three appearance potentials are associated with the three most likely modes of decomposition of CX_4 to give C^+:

$$e^- + CX_4 \longrightarrow C^+ + 2X_2 + 2e^- \qquad (g)$$

$$e^- + CX_4 \longrightarrow C^+ + X_2 + 2X + 2e^- \qquad (h)$$

$$e^- + CX_4 \longrightarrow C^+ + 4X + 2e^- \qquad (i)$$

from which are obtained:

$$(g) \sim A_1(C^+) = I(C) + \Sigma D_4(CX_4) - 2D(X_2) \qquad (2.5)$$

$$(h) \sim A_2(C^+) = I(C) + \Sigma D_4(CX_4) - D(X_2) \qquad (2.6)$$

$$(i) \sim A_3(C^+) = I(C) + \Sigma D_4(CX_4) \qquad (2.7)$$

where $\Sigma D_4(CX_4) = D(CX_3\text{-}X) + D(CX_2\text{-}X) + D(CX\text{-}X) + D(C\text{-}X)$. Combination of the relevant experimental measurements with $I(C)$ and $D(X_2)$ then yields the data drawn up in Table 10c.

TABLE 10c

	By Equn. (2.5)		By Equn. (2.6)	
X	$\Sigma D_4(CX_4)$ eV.	D(C-X) eV.	$\Sigma D_4(CX_4)$ eV.	D(C-X) eV.
F	19.77±0.05	4.69±0.2	19.76±0.05	4.68±0.2
Cl	13.23±0.05	4.30±0.2	13.26±0.05	4.33±0.2
Br	11.59±0.1	3.64±0.25	11.48±0.05	3.53±0.2

Table 10 c Continued/

/Table 10c (Ctd).

By Equn. (2.7)

X	$\Sigma D_4(CX_4)$ eV.	D(C-X) eV.
F	19.63±0.1	4.8±0.3
Cl	13.23±0.1	4.2±0.3
Br	11.53±0.1	3.6±0.3

It will be seen from the foregoing that all the appearance potentials observed in the CX_4 series can be explained by a common type of dissociative process i.e. there is a unity in the nature of the successive bond dissociation mechanisms. In addition consideration of the summary of bond energies, given in Table 11, shows that they form a reasonably self consistent set, and, where appropriate, are equal to one another within the limits of experimental accuracy. Also, our bond energies are in good agreement with those quoted in the literature. No other mechanism or set of mechanisms yield as good consistency or agreement, hence we can say that the modes of decompostion selected are probably correct.

TABLE 11

Bond dissociation energies * in the CX_4 series(X≡F,Cl,Br)

Bond	Dissociation Energy eV. X≡F	X≡Cl	X≡Br
$D(CX_3-X)$	5.25±0.1	3.12±0.1	2.16±0.05
$D(CX_2-X)$	(5.28±0.25 5.35±0.3	2.36±0.25 2.4 ±0.3	2.04±0.2 2.04±0.25
D(CX-X)	(4.55±0.3 4.2 ±0.4	3.45±0.3 3.5 ±0.4	3.65±0.3 3.7 ±0.4
D(C-X)	4.69±0.2 (4.68±0.2 4.8 ±0.3	4.3± 0.2 4.33±0.2 4.2 ±0.3	3.64±0.25 3.53±0.2 3.6 ±0.3

* Where two or three values are bracketted together, they have been calculated assuming different mechanisms.

The Latent Heat of Sublimation of Carbon.

The latent heat of carbon is obtained by means of the following thermochemical cycle:

$C(s) + 2X_2(g) \longrightarrow CX_4$	$\Delta H_f(CX_4)$
$C(s) \longrightarrow C(g)$	L_c
$2X_2(g) \longrightarrow 4X(g)$	$2D(X_2)$
$C(g) + 4X(g) \longrightarrow CX_4$	$-\Sigma D_4(CX_4)$

whence $L_c = \Sigma D_4(CX_4) + \Delta H_f(CX_4) - 2D(X_2)$

In Table 12, the required data has been collected and L_c calculated according to the above relationship.

TABLE 12.

$\Delta H_f(CX_4)(g)$ eV.	-9.45±0.00	-1.06	-0.39
$\Sigma D_4(CX_4)$ eV.	19.76±0.05	13.26±0.05	11.48±0.05
$D(X_2)$ eV.	1.56	2.48	1.97
L_c eV.	7.19±0.1	7.24±0.1	7.15±0.1

The average value of L_c is 7.2±0.2 eV. Comparrison of this with the spectroscopically permitted values shows that L_c = 7.386 eV. is probably correct. This is the maximum allowable while the error in the determination of the present value of L_c is not sufficiently large to include the next lower value, 6.13 eV., provided, of course, that the assumptions made earlier with regard to kinetic and electronic excitational energy are justified.

(b) The Heat of Dissociation of Nitrogen.

It has been shown earlier how an estimate of the heat of dissociation of nitrogen may be made from a knowledge of the heat of atomization of ammonia using techniques and arguments similar to those described above.

Apparatus*Method.

The measurement of appearance and ionization potentials was conducted in exactly the same manner as outlined for CX_4 above. The radicals NH_2 and NH were obtained by pyrolisis of NH_3 also in the way described above for the production of halocarbon radicals.

Material.

The ammonia was obtained by dropping the concentrated aquious solution (S.G. = 0.88) into caustic soda pellets, drying the evolved gas over solid NaOH and finally condensing in liquid air. This sample was used without further purification. Mass spectral analysis, as before, did not detect any significant amounts of impurity.

Results.

The values of appearance and ionization potentials observed in this work are entered in Table 13, together

with the corresponding literature values where available. The uncertainties quoted are standard deviations.

TABLE 13

Appearance and ionization potentials of NH_x from NH_3 .

Appearance Potentials eV.			Species	I.P. eV.
Species	Observed	Literature		
NH_3^+	10.43±0.05	*	NH_3	10.43±0.05
NH_2^+	17.73±0.1	15.7±0.1	NH_2	13.14±0.05
NH^+	17.1 ±0.1	19.4±0.5	NH	13.10±0.05
	21.6 ±0.1	-		
N^+	22.2 ±0.1	25.0±0.5		
	24.1 ±0.1	28.1±0.7		
	26.65±0.1	-		
	28.6 ±0.1	-		

Ionization Potential (Lit.)	
Species	I.P. eV.
NH_2	11.4 ±0.1 (113)

* Several values for $I(NH_3)$ have been put forward. In chronological order they are 10.5±0.1 eV. (49): 10.42±0.05 eV. (58): 10.25±0.1 eV. (59): 10.07±0.1 eV. (60).

DISCUSSION.

All the dissociative processes to be given below refer to ions formed without kinetic energy. Half-beam width measurements (31) of the ions NH_2^+, NH^+ and N^+ were carried out as in the previous experiments. Once again there was no appreciable defocussing of the ion beam at the collector slit indicating that there was no significant kinetic energy associated with the production of these particular ions.

Ionization Processes.

1. NH_2^+: It is considered that the most likely way in which NH_2^+ is produced is by the straightforward dissociation

$$e^- + NH_3 \longrightarrow NH_2^+ + H + 2e^-$$

assuming that E_k and E_e are zero. This leads to the equation

$$A(NH_2^+) = I(NH_2) + D(NH_2\text{-}H)$$

which on substitution yields $D(NH_2\text{-}H) = 4.59 \pm 0.15$ eV. This is in good agreement with the evidence obtained from electron impact studies on ammonia (49) hydrazine (113) and from the pyrolisis of hydrazine (61) and benzylamine (61)

the values being 4.50 eV., 4.60 eV., 4.34 eV. and 4.51 eV. respectively. This tends to exclude the alternative mechanism

$$e^- + NH_3 \longrightarrow NH_2^+ + H^- + e^-$$

which would serve to increase the above estimate of $D(NH_2\text{-}H)$ by 0.75 eV. which is the electron affinity of hydrogen.

2. $\underline{NH^+}$: There are two mechanisms which can give rise to this ion, namely (a) and (b).

$$e^- + NH_3 \longrightarrow NH^+ + H_2 + 2e^- \qquad (a)$$

$$e^- + NH_3 \longrightarrow NH^+ + 2H + 2e^- \qquad (b)$$

Two appearance potentials have been recorded for NH^+. The energy difference between them, 4.5 eV., is close to the heat of dissociation of hydrogen, $D(H_2) = 4.48$ eV., which suggests that the lower appearance potential (A_1) should correspond with reaction (a) while the higher, $A_2(NH^+)$ should refer to (b). Hence the following relationships are obtained:

$$(a) \sim A_1(NH^+) = I(NH) + \Sigma D_2(NH_3) - D(H_2) \qquad (3.1)$$

$$(b) \sim A_2(NH^+) = I(NH) + \Sigma D_2(NH_3) \qquad (3.2)$$

where $\Sigma D_2(NH_3) = D(NH_2\text{-}H) + D(NH\text{-}H)$.

Substitution of the appropriate data then gives

(3.1) $\Sigma D_2(NH_3) = 8.5 \pm 0.15$ eV. whence $D(NH\text{-}H) = 8.5\text{-}4.6$

(3.2) $\Sigma D_2(NH_3) = 8.5 \pm 0.15$ eV. $= 3.9 \pm 0.3$ eV.

Altshuller (62) has calculated a value of $D(NH\text{-}H) = 3.82$ eV. with which this estimate is in excellent agree-

:ment. The other possible mechanisms

$$e^- + NH_3 \longrightarrow NH^+ + H + H^- + e^-$$

$$e^- + NH_3 \longrightarrow NH^+ + 2H^-$$

would imply that

$$A(NH^+) = I(NH) + \Sigma D_2(NH_3) - nEA(H) \qquad (3.3)$$

where n is 1 and 2 respectively. This gives, on substit-:ution of $A_1(NH^+)$, D(NH-H) = 0.15 and 0.9 eV. by (3.3) (n = 2 and 1 respectively) while $A_2(NH^+)$ leads to D(NH-H) = 5.4 eV. and 4.65 eV. The first two values are obviously too low while the second pair are appreciably higher than Altshuller's estimate. In addition, if D(NH-H) = 4.7 eV., D(N-H) would then require to be about 2.7 eV. which is in serious disagreement with reliable spectroscopic studies.

It should be noted that Altshuller based his calcul-:ation on $D(N_2)$ = 9.756 eV., therefore the measured D(NH-H) tends to confirm, within the limits of error, this value of $D(N_2)$.

3. $\underline{N^+}$: The ionization efficiency curve of N^+ contains four distinct breaks. The differences in energy between A_1 and the other three are 1.9 eV., 4.45 eV., and 6.4 eV. respe ctively. The difference $A_3 - A_1$ is in good agree-:ment with $D(H_2)$ = 4.48 eV., and since NH^+ could be produc-:ed with the accompaniment of either H_2 or 2H, A_1 and A_3 are thought to refer to the mechanisms (c) and (d) respective-:ly

$$e^- + NH_3 \longrightarrow N^+(^3P) + H_2 + H + 2e^- \quad (c)$$

$$e^+ + NH_3 \longrightarrow N^+(^3P) + 3H + 2e^- \quad (d)$$

hence the equations(3.4) and (3.5) are obtained

$$(c) \sim A_1(N^+) = I(N) + \Sigma D_3(NH_3) - D(H_2) \quad (3.4)$$

$$(d) \sim A_3(N^+) = I(N) + \Sigma D_3(NH_3) \quad (3.5)$$

where $\Sigma D_3(NH_3) = D(NH_2\text{-}H) + D(NH\text{-}H) + D(N\text{-}H)$.

Substitution of A_1 and A_3 in the appropriate equation then gives:

(3.4). $\Sigma D_3(NH_3)$ = 12.2±0.1 eV. whence D(N-H) = 3.7±0.25 eV.

(3.5). $\Sigma D_3(NH_3)$ = 12.17±0.1eV. whence D(N-H) = 3.67±0.25eV.

Using spectroscopic data, Pannetier and Gaydon (63) have found D(N-H) = 3.8 eV. with which our estimates are in good agreement. For similar reasons to those given for the formation of NH^+, mechanisms involving H^- ions cannot be applied to A_1 and A_3.

Now A_2 and A_4 occur at an energy of 1.9 eV. greater than A_1 and A_3 respectively. If it is assumed that N^+ ions are formed without kinetic energy, (and our method of testing would have detected this amount) the most likely possibilty is that N^+ is produced in an electronically excited state. The ground state of N^+ is the ^3P which is separated from the next highest level, the ^1D, by 1.9 eV. (22b). Hence it is possible to assign A_2 and A_4 to mechanisms (f) and (g) respectively.

$$e^- + NH_3 \longrightarrow N^+(^1D) + H_2 + H + 2e^- \quad (f)$$

$$e^- + NH_3 \longrightarrow N^+(^1D) + 3H + 2e^- \quad (g)$$

for which are deduced

$$(f) \sim A_2(N^+) = I(N) + \Sigma D_3(NH_3) - D(H_2) + E_e \qquad (3.6)$$

$$(g) \sim A_4(N^+) = I(N) + \Sigma D_3(NH_3) + E_e \qquad (3.7)$$

where E_e = 1.9 eV, the separation of the ^3P and ^1D levels of N^+. Whence

(3.6): $\Sigma D_3(NH_3)$ = 12.2±0.1 eV. yielding D(N-H) = 3.7±0.25 eV.

(3.7): $\Sigma D_3(NH_3)$ = 12.2±0.1 eV. yielding D(N-H) = 3.7±0.25 eV.

The close agreement of the values of $\Sigma D_3(NH_3)$ by all four mechanisms is strongly suggestive that the correct ones have been selected. In addition, all four estimates of D(N-H) are in close concordance with spectroscopic results. On the other hand, dissociative processes involving H^- ions give bond energies which are in poor agreement with one another and with results of other workers, while at the same time they are out-with the general trend of those heats of dissociation already established.

The heat of formation $\Delta H_f(NH_3)$ and the heat of atomization $\Sigma D_3(NH_3)$ of ammonia are related to $D(N_2)$ by the cycle:

$\frac{1}{2}N_2(g) + 1\frac{1}{2}H_2(g) \longrightarrow NH_3(g)$	$-\Delta H_f(NH_3)$ (g)
$\frac{1}{2}N_2(g) \longrightarrow N(g)$	$\frac{1}{2}D(N_2)$
$1\frac{1}{2}H_2(g) \longrightarrow 3H(g)$	$1\frac{1}{2}D(H_2)$
$N(g) + 3H(g) \longrightarrow NH_3(g)$	$-\Sigma D_3(NH_3)$

Whence $D(N_2) = 2\Sigma D_3(NH_3) - 2\Delta H_f(NH_3) - 3D(H_2)$.

Taking $\Sigma D_3(NH_3)$ = 12.2±0.1 eV, $\Delta H_f(NH_3)$ = -0.48 eV and $D(H_2)$ = 4.48 eV. $D(N_2)$ = 10.0± 0.1 eV. is obtained.

This value must be regarded as the minimum obtainable from our experiment, since any other dissociative mechanism chosen leads to improbably high values of $\Sigma D_3(NH_3)$ and hence even higher values of $D(N_2)$. Also, the bond energies calculated in this work are in good agreement with those quoted by other workers, hence the present value of ΣD_3 must be of the correct order of magnitude. The experimental uncertainty is certainly insufficient to allow of consideration of the next lowest permitted value of $D(N_2) = 7.38$ eV. Hence it is considered that $D(N_2) = 9.756$ eV. is most likely to be correct.

[illegible] selected for study since they were readily available, [illegible] high state of purity, or in such a condition [illegible] be readily purified. In addition, no electr[illegible] had been reported on CH_2X_2 or CHX_3 althou[illegible] CH_3X had been studied by previous workers (see Intr[illegible]

The Electron Impact Studies On- CH_3X, CH_2X_2, and CHX_3 (X ≡ Cl, Br).

From a consideration of the work described above, it is a logical step to attempt to extend the dissociative mechanisms proposed for the decomposition of CX_4(X ≡F,Cl,Br) to account for the appearance potentials of the positive ions derived from the partially halogenated methanes, and to discover whether the observations are compatible with L_c = 7.386 eV. as proposed from the results of the previous experiments. Accordingly the six compounds above were selected for study since they were readily available, either in a high state of purity, or in such a condition that they could be readily purified. In addition, no electron impact work had been reported on CH_2X_2 or CHX_3 although CH_3X had been studied by previous workers (see Introduction).

EXPERIMENTAL.

1. Apparatus and Method:

The apparatus and technique have been previously described above, but some modification was necessary for the production of CHX_2 radicals. In these cases, a mixture of CH_2X_2 and CCl_4 vapours were passed over the heated tungsten wire. The CCl_4 decomposed to give Cl atoms which abstracted a hydrogen atom from CH_2X_2 to give CHX_2. For further examples see Steacie (65). The required radicals were obtained only in low concentration but there were a sufficient number produced for the determination of the ionization potential. CHCl radicals were obtained in good yield by the pyrolysis of $CHClBr_2$ vapour. The remaining radicals were obtained, mostly in rather poor yield, by straightforward pyrolysis of the parent compound.

2. Materials:

$CHCl_3$, CH_3Cl and CH_3Br were A.R. grade and used without further pufification. CH_2Cl_2, CH_2Br_2, $CHBr_3$ and $CHClBr_2$ were reagent grade. CH_2Cl_2 was distilled several times prior to use, the middle fraction of each distillate being retained. The bromo compounds were washed with a mixture of K I and $Na_2S_2O_3$ solutions followed by water to remove free bromine. The liquids were then dried over $CaCl_2$, and finally distilled in vacuo. In each case, the mass spectrum showed no significant amounts of impurity.

RESULTS.

The results obtained in the course of these investigations are entered in Tables 14a-14d. The uncertainties attached to each value are standard deviations. Literature values are given in Table 14e for comparrison.

TABLE 14a

Appearance potentials of positive ions derived from CH_3X.

Species	Appearance Potential eV. X ≡ Cl	Appearance Potential eV. X ≡ Br
CH_3^+	13.35±0.05	13.05±0.05
CH_2^+	15.00±0.05	15.28±0.05
	19.5 ±0.1	19.15±0.05
	19.1 ±0.1	18.85±0.05
	22.1 ±0.1	19.70±0.05
CH^+	23.7 ±0.2	21.8 ±0.1
	26.6 ±0.2	23.4 ±0.1
		26.4 ±0.1
		22.4 ±0.1
C^+	23.0 ±0.1	23.2 ±0.1
	27.5 ±0.1	26.9 ±0.1
	28.4 ±0.1	27.75±0.1
	32.8 ±0.2	28.5 ±0.1
		32.25±0.1

TABLE 14b

Appearance potentials of positive ions derived from CH_2X_2.

Species	Appearance Potential eV. X ≡ Cl	X ≡ Br
CH_2X^+	12.89±0.05	10.93±0.05
CH_2^+	16.10±0.05	14.60±0.05
	18.55±0.05	16.65±0.05
CHX_2^+	13.32±0.05	-
CX_2^+	16.05±0.1	-
	20.6 ±0.1	-
CH^+	18.50±0.05	18.25±0.05
	20.37±0.05	19.90±0.05
	21.5 ±0.1	21.15±0.05
	22.9 ±0.1	22.0 ±0.1
	23.55±0.1	22.9 ±0.1
	25.9 ±0.1	24.9 ±0.1
		21.00±0.05
C^+	22.00±0.05	22.00±0.1
	24.05±0.05	23.5 ±0.1
	26.55±0.1	25.5 ±0.1
	27.45±0.2	26.4 ±0.2
	29.4 ±0.2	27.15±0.2
	31.9 ±0.2	28.85±0.2
		30.8 ±0.2

TABLE 14c

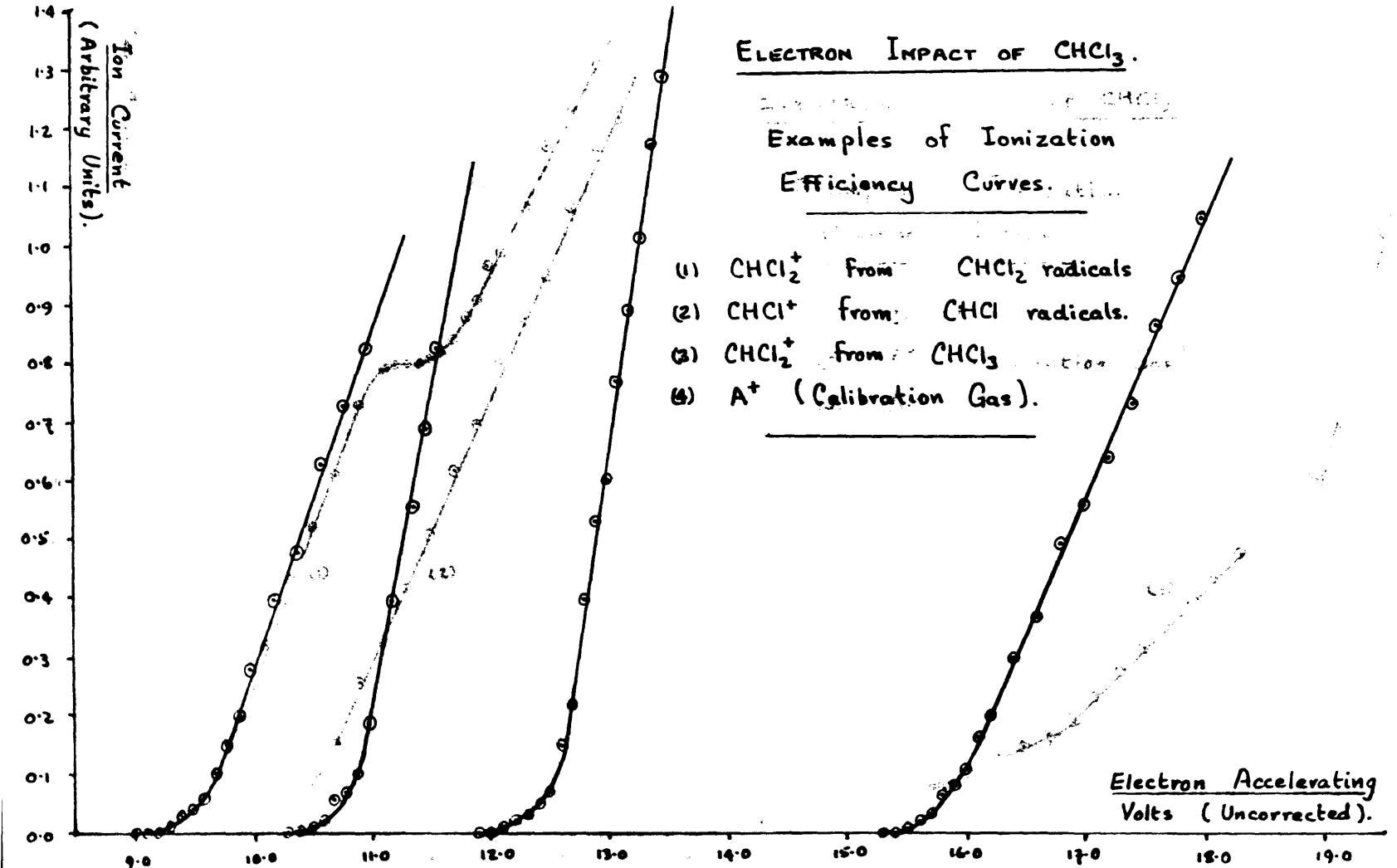
Appearance potentials of positive ions derived from CHX_3.

Species	Appearance Potential eV. X ≡ Cl	X ≡ Br
CHX_2^+	12.43±0.05	10.80±0.05
CHX^+	14.87±0.05	14.67±0.05
	17.30±0.05	16.62±0.05
CX_2^+	15.3 ±0.1	-
	19.8 ±0.1	-
CH^+	19.65±0.05	18.7 ±0.1
	21.95±0.1	20.6 ±0.1
	22.7 ±0.1	21.75±0.1
	24.95±0.1	23.7 ±0.1
		20.50±0.05
C^+	23.15±0.05	22.25±0.05
	25.76±0.05	24.30±0.05
	28.3 ±0.1	25.8 ±0.1
	30.8 ±0.1	27.55±0.1
		29.55±0.1

TABLE 14d

Ionization potentials of radicals from CH_2X_2 and CHX_3.

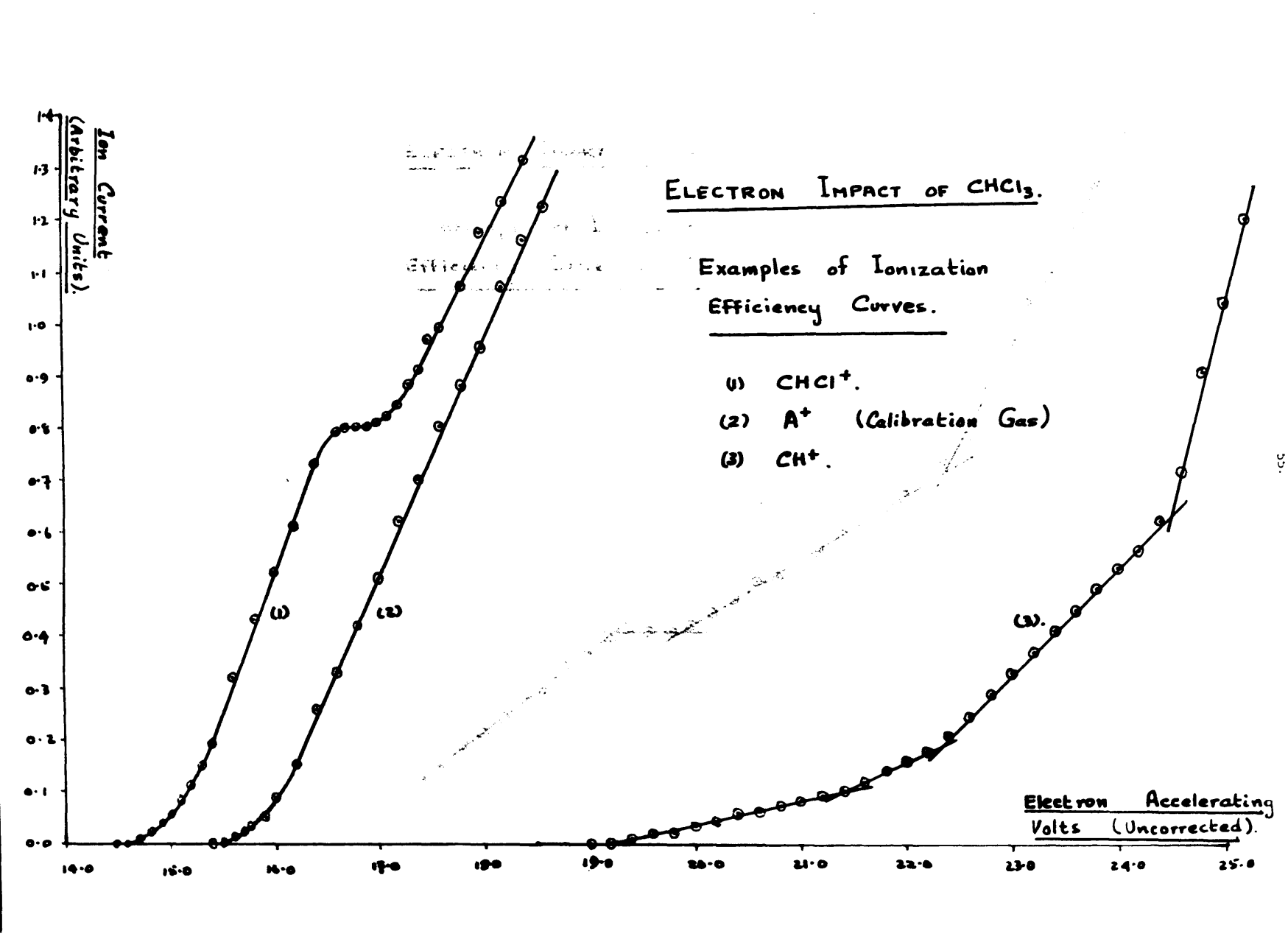
Species	Ionization Potential eV. X ≡ Cl	X ≡ Br
CH_2X	9.7 ±0.1	8.35±0.1
CHX_2	9.55±0.1	8.05±0.1
CHX	10.95±0.1	11.4 ±0.1



Electron Impact of $CHCl_3$.

Examples of Ionization Efficiency Curves.

(1) $CHCl_2^+$ from $CHCl_2$ radicals
(2) $CHCl^+$ from $CHCl$ radicals.
(3) $CHCl_2^+$ from $CHCl_3$
(4) A^+ (Calibration Gas).



Electron Impact of $CHCl_3$.

Examples of Ionization Efficiency Curves.

(1) $CHCl^+$.

(2) A^+ (Calibration Gas)

(3) CH^+.

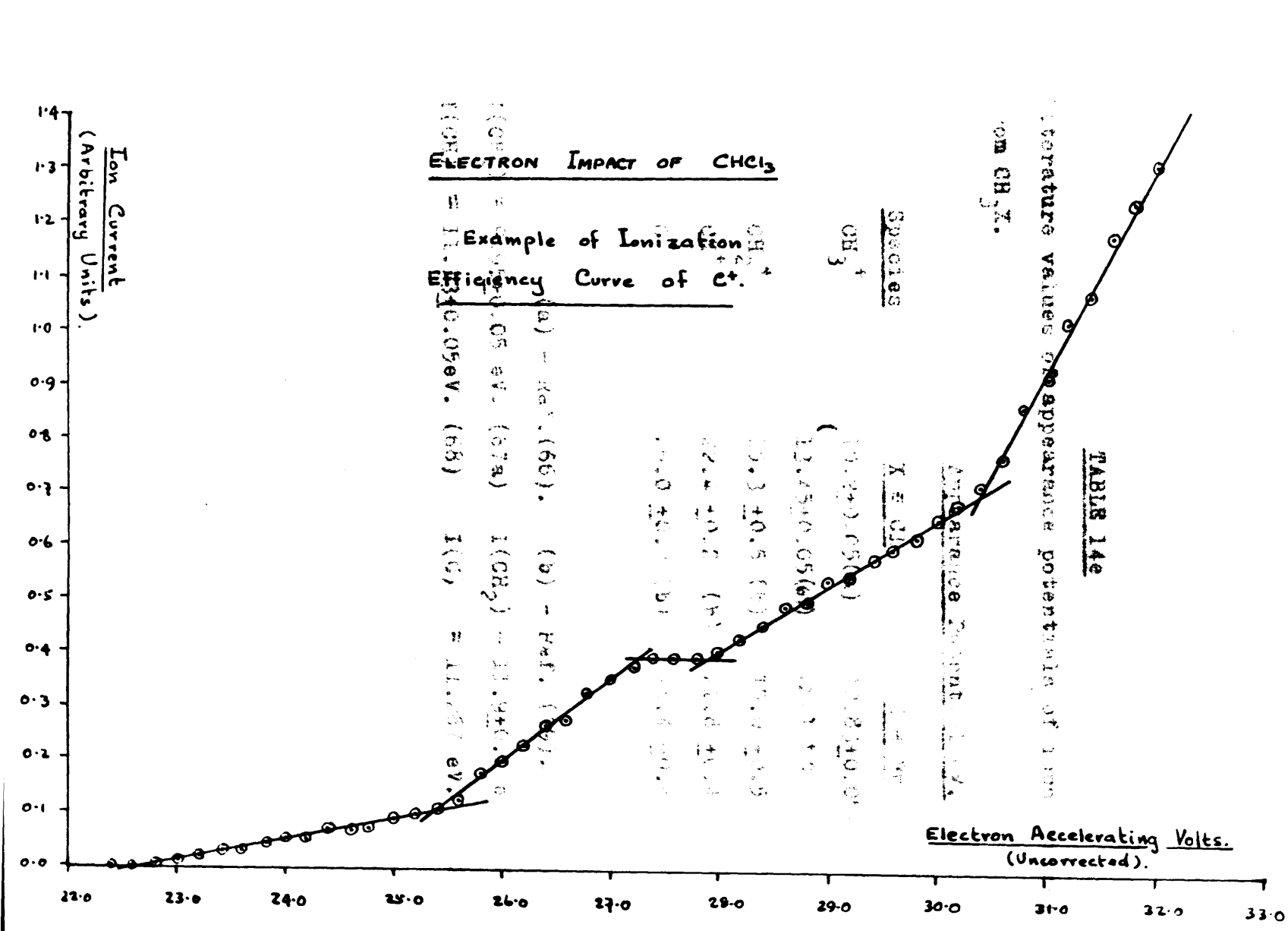

ELECTRON IMPACT OF $CHCl_3$
Example of Ionization Efficiency Curve of C^+.
Ion Current (Arbitrary Units).
Electron Accelerating Volts. (Uncorrected).
1·4
1·3
1·2
1·1
1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0·0
22·0
23·0
24·0
25·0
26·0
27·0
28·0
29·0
30·0
31·0
32·0
33·0

TABLE 14e

TABLE 14e

Literature values of appearance potentials of ions derived from CH_3X.

Species	Appearance Potential eV. X ≡ Cl	X ≡ Br
CH_3^+	10.2±0.05(a) 13.45±0.05(67)	12.83±0.05(67) 12.9 ±0.1 (a)
CH_2^+	15.3 ±0.5 (b)	15.0 ±0.5 (b)
CH^+	22.4 ±0.2 (b)	21.8 ±0.4 (b)
C^+	26.0 ±0.2 (b)	25.4 ±0.4 (b)

(a) - Ref.(66). (b) - Ref. (29).

$I(CH_3)$ = 9.95±0.05 eV. (67a) $I(CH_2)$ = 11.9±0.1 eV. (32)

$I(CH)$ = 11.13±0.05eV. (68) $I(C)$ = 11.267 eV. (22c)

DISCUSSION.

Since CH_3Cl and CH_3Br have been studied previously (29), (66), (67), it is convenient to discuss these two compounds first. Also, the bond energies $D(CH_2-H)$, D(CH-H) and D(C-H) have been obtained from measurements performed on methane (31). Hence it is possible to compare these results with our own conclusions.

A search for excess kinetic energy associated with the production of C^+ ions from the six compounds was conducted as described for CX_4. No detectable broadening of the ion beam was observed hence it was decided that the ions produced in the present studies have little or no translational energy. This is in agreement with the observations of Morrison and Stanton (69).

Dissociation Processes in CH_3X (X≡Cl,Br).

1. CH_3^+: As in previous cases, the initial dissociation is considered to be

$$e^- + CH_3X \longrightarrow CH_3^+ + X + 2e^- \qquad (a)$$

whence $$A(CH_3^+) = I(CH_3) + D(CH_3-X) \qquad (4.1)$$

Substitution of the measured $A(CH_3^+)_{CH_3Cl}$ and $A(CH_3^+)_{CH_3Br}$ gives $D(CH_3-Cl) = 3.4 \pm 0.1$ eV. and $D(CH_3-Br) = 3.1 \pm 0.1$ eV. These two results are in excellent agreement with the

thermochemically derived $D(CH_3-Cl)$ = 3.46 eV. and $D(CH_3-Br)$ = 2.90 eV. obtained by Szwarc (70) by means of kinetic studies. $D(CH_3-X)$ have also been measured, using electron impact methods by Lossing (67b) and Dibeler (66) and their co-workers. The acceptance of the alternative mechanism (b):

$$e^- + CH_3X \longrightarrow CH_3^+ + X^- + e^- \qquad (b)$$

would require $D(CH_3-X)$ = 7.22 and 6.63 eV. for X ≡ Cl and Br respectively - both being obviously too high.

2. $\underline{CH_2^+}$: Two values of $A(CH_2^+)$ have been observed for each CH_3X. These are thought to correspond to the two mechanisms (c) and (d) below.

$$e^- + CH_3X \longrightarrow CH_2^+ + HX + 2e^- \qquad (c)$$

$$e^- + CH_3X \longrightarrow CH_2^+ + H + X + 2e^- \qquad (d)$$

which would lead to equations (4.2) and (4.3).

$$(c) \sim A_1(CH_2^+) = I(CH_2) + \Sigma D_2(CH_3X) - D(H-X) \qquad (4.2)$$

$$(d) \sim A_2(CH_2^+) = I(CH_2) + \Sigma D_2(CH_3X) \qquad (4.3)$$

where $\Sigma D_2(CH_3X) - D(CH_3-X) + D(CH_2-H)$. If the appropriate appearance potentials are combined with the known values of $I(CH_2)$ and D(H-X) the results quoted in Table 15 are obtained.

TABLE 15

	$\Sigma D_2(CH_3X)$ eV.		$D(CH_2-H)$ eV.	
Equn.	X ≡ Cl	X ≡ Br	X ≡ Cl	X ≡ Br
(4.2)	7.55±0.15	7.13±0.15	4.15±0.2	4.03±0.25
(4.3)	7.6 ±0.2	7.25±0.15	4.20±0.25	4.15±0.25
(4.4)	6.92±0.15	6.91±0.15	3.52±0.2	3.64±0.25

There is, of course, the possibilty that A_1 refers to the formation of CH_2^+ accompanied by X^- and H rather than HX. If this were the dase, equation (4.4) would apply.

$$A_1(CH_2^+) = I(CH_2) + \sum D_2(CH_3X) - EA(X) \qquad (4.4)$$

The values of $\sum D_2(CH_3X)$ and $D(CH_2\text{-}H)$ calculated according to (4.4) are also included in Table 15a. As may be seen, the results obtained from (4.2) and (4.3) are in much bett-:er agreement than those from (4.3) and (4.4). Also, it is unreasonable to suppose that CH_2^+ is formed together with X^- while CH_3^+ is not. On the other hand, the results from (4.4) are in better agreement with values of $D(CH_2\text{-}H)$ = 3.45±0.2 eV. obtained by McDowell and Warren (31), and 3.75±0.3 eV. preferred by Langer, Hipple and Stevenson (32), both from studies on methane. (However, see Introduction for an alternative interpretation of the observations of these workers.) In addition, evidence as to the mechanism of the reaction $CH_2Cl_2 + 2Na \longrightarrow CH_2 + 2NaCl$. obtained by Bawn and Dunning (71) has enabled Laidler and Casey (72) to derive $D(CH_2\text{-}H)$ = 3.9 eV. which is in good agreement with the results from (4.2) and (4.3). Hence it is concluded that the dissociative mechanisms (c) and (d) above are the correct ones and that $D(CH_2\text{-}H)$ = 4.1±0.2 eV.

3. $\underline{CH^+}$: The most likely modes of decomposition of CH_3X to give CH^+ are (e), (f) and (g).

$$CH_3X + e^- \longrightarrow CH^+ + H_2 + X + 2e^- \qquad (e)$$

$$CH_3X + e^- \longrightarrow CH^+ + HX + H + 2e^- \qquad (f)$$

$$CH_3X + e^- \longrightarrow CH^+ + 2H + X + 2e^- \qquad (g)$$

Four appearance potentials are observed for CH^+ from CH_3Cl of which the first and third are separated by 4.6 ± 0.3 eV. Since $D(H_2) = 4.52$ eV. and $D(H-Cl) = 4.45$ eV., both are within the limits of accuracy of A_3-A_1, and hence $A_1(CH^+)_{CH_3Cl}$ can apply to either process (e) or (f) while $A_3(CH^+)_{CH_3Cl}$ is assigned to (g).

On the other hand, of the five appearance potentials observed for CH^+ from CH_3Br, $A_4-A_1 = 4.55\pm0.15$ eV. and $A_4-A_2 = 3.7\pm0.15$ eV. These correspond respectively with $D(H_2) = 4.52$ eV. and $D(H-Br) = 3.75$ eV. Thus $A_1(CH^+)_{CH_3Br}$ can be taken to refer to (e), $A_2(CH^+)_{CH_3Br}$ to (f) and $A_4(CH^+)_{CH_3Br}$ to (g). In the case of CH_3Cl, it is probable that CH^+ is formed together with both H_2 and HCl molecules, but since the difference in $A(CH^+)$ for the two processes would be only 0.1 eV., the two breaks in the ionization efficiency curve of CH^+ would not be resolved.

The above three decomposition processes lead to the equations:

$$(e) \sim A_1(CH^+)_{CH_3Cl} = I(CH) + \Sigma D_3(CH_3Cl) - D(H_2) \qquad (4.5)$$

$$(g) \sim A_3(CH^+)_{CH_3Cl} = I(CH) + \Sigma D_3(CH_3Cl) \qquad (4.6)$$

$$(e) \sim A_1(CH^+)_{CH_3Br} = I(CH) + \Sigma D_3(CH_3Br) - D(H_2) \qquad (4.7)$$

$$(f) \sim A_3(CH^+)_{CH_3Br} = I(CH) + \Sigma D_3(CH_3Br) - D(H-Br) \qquad (4.8)$$

$$(g) \sim A_4(CH^+)_{CH_3Br} = I(CH) + \Sigma D_3(CH_3Br) \qquad (4.9)$$

Substitution of the appropriate data then gives the results shown in Table 15b.

TABLE 15b

	$\Sigma D_3(CH_3X)$ eV.		D(CH - H) eV.	
Equations.	X ≡ Cl	X ≡ Br	X ≡ Cl	X ≡ Br
(4.5) (4.7)	12.5 ±0.15	12.24±0.1	4.9±0.3	5.1±0.3
(4.8)	-	12.32±0.1	-	5.2±0.3
(4.6) (4.9)	12.57±0.15	12.27±0.15	5.0±0.3	5.1±0.3

Once again the results are concordant, but the average value of D(CH-H) = 5.1±0.3 eV. is significantly higher than those proposed by previous workers (31,32). However, no other set of dissociative mechanisms fit the five appearance potentials so well; in particular processes involving negative ions do not produce such close mutual agreement within the calculated bond energies for all the observed appearance potentials.

The next problem is the asignment of $A_2(CH^+)$ and $A_4(CH^+)$ of CH_3Cl and $A_3(CH^+)$ and $A_5(CH^+)$ of CH_3Br to some suitable decomposition process. In equations (4.5) - (4.9) above, it was assumed that the fragments were produced in their electronic ground state and without kinetic energy. If excess energy E were present, equations of the form:

$$A(CH^+) = I(CH) + \Sigma D_3(CH_3X) - D^{(H_2)}_{(HX)} + E \qquad (4.10)$$

$$A(CH^+) = I(CH) + \Sigma D_3(CH_3X) + E \qquad (4.11)$$

must be used. The energy differences $A_4(CH^+) - A_2(CH^+)$ of CH_3Cl = 4.5±0.3 eV. and $A_5(CH^+) - A_3(CH^+)$ of CH_3Br = 4.6±0.2 eV. both probably correspond to $D(H_2)$. This implies that the lower of each pair of appearance potentials should be applied to equation (4.10) and the higher to (4.11). If then, under this assumption, the average values for $\sum D_3(CH_3X)$ = 12.55±0.15 eV. for X ≡ Cl and $\sum D_3(CH_3X)$ = 12.28±0.15 eV. for X ≡ Br are substituted in the above equations we obtain E = 3.0±0.1 eV. for both CH_3Cl and CH_3Br.

This value of E is, of course, dependent of the accuracy of the measured $\sum D_3(CH_3X)$, but it is possible to calculate a value for $\sum D_3(CH_3X)$ from the equation:

$$L_c = \sum D_3(CH_3X) + D(C\text{-}H) - 1\tfrac{1}{2}D(H_2) - \tfrac{1}{2}D(X_2) + \Delta H_f(CH_3X)$$

D(C-H) = 3.47 eV. is known from spectroscopy (3,2), $D(H_2)$, $D(X_2)$ and $\Delta H_f(CH_3X)$ are also well established (see appendix), hence assuming a value of L_c, an estimate of $\sum D_3(CH_3X)$ independent of mass spectral measurement is obtained. The selection of L_c = 7.386 eV. gives $\sum D_3(CH_3Cl)$ = 12.79 eV. and $\sum D_3(CH_3Br)$ = 12.05 eV. both of which are in good agreement with the measured values. This shows that so far, the dissociative mechanisms chosen and the results obtained therefrom support the highest value of L_c. The choice of the next lowest permitted L_c = 6.13 eV. would result in $\sum D_3(CH_3X)$ = 11.53 eV. and 10.79 eV. respectively for X ≡Cl and Br.

Substitution of the calculated values of $\sum D_3(CH_3X)$

in equation (4.11) above then gives $E(CH_3Cl)$ = 2.7±0.2 eV. and $E(CH_3Br)$ = 3.2±0.2 eV. these two values of E depend only on the measured $A(CH^+)$ and are independent of any est-:imate of D(CH-H).

The simplest interpretation of the presence of excess energy is that it is associated with a common step in the reactions giving CH^+ from both CH_3Cl and CH_3Br. Moreover, since E is sensibly constant for both compounds, it is un-:likely that the energy is kinetic, since it is unreasonable to suppose that two different compounds decomposed to give fragments of differing masses (in one case a chlorine atom, in the other a bromine) will have associated with these fragments nearly identical quantities of translational en-:ergy. Also, Morrison and Stanton (69) have shown that the kinetic energy of the ions derived from CH_3X is negli-:gibly small which is in agreement with our own observations. It is therefore concluded that the excess energy represent-:ed by E is electronic in character. Furthermore, since the values of $D(CH_3-X)$ and $D(CH_2-H)$, calculated above on the assumption that the products of dissociation are in their ground states, are in good agreement with the obser-:vations of previous workers, it is probable that the CH^+ ion is produced in an excited state.

One possibility is that E corresponds with the known (3) transition $CH^+(X.^1\Sigma^+ \longrightarrow A.^1\Pi)$ = 2.99 eV. Such a conclusion had already been arived at by Langer, Hipple

and Stevenson (32) (although they used a somewhat diffenent mechanism) from a study of the decomposition of CH_3 and CH_2 radicals. Another possibility is that the energy is mostly vibrational, arising in the course of the rather ex-:tensive fragmentation of the molecule. Such a suggestion would be consistent with observation only if this energy term were located around one or more of the C-H bonds as these are commond to both molecules.

4. $\underline{C^+}$: If it is assumed to begin with that the pro-:ducts of dissociation are in their electronic ground state, four mechanisms of decomposition are possible:

$$e^- + CH_3X \longrightarrow C^+ + H_2 + HX + 2e^- \qquad (h)$$

$$e^- + CH_3X \longrightarrow C^+ + H_2 + H + X + 2e^- \qquad (j)$$

$$e^- + CH_3X \longrightarrow C^+ + 2H + HX + 2e^- \qquad (k)$$

$$e^- + CH_3X \longrightarrow C^+ + 3H + X + 2e^- \qquad (l)$$

For similar reasons to those already considered for CH^+, processes involving negative ion formation are not accept-:able.

It has been decided that the lowest appearance potent-:ial $A_1(C^+)$ in each case refers to (j) above rather than (h). Substitution of A_1 in (j) yields D(C-H) = 3.70±0.25 eV. for CH_3Cl, and 3.37±0.25 eV. for CH_3Br. The second appearance potential $A_2(C^+)$ of CH_3Cl occurs at 4.5±0.2 eV. above the first, while $A_2(C^+)$ and $A_3(C^+)$ of CH_3Br lie 3.7 eV. apart and $A_3(C^+)$ is 4.5 eV. above $A_1(C^+)$. From a consideration of these observations and the precedents set

in the discussion of CH^+ above, it is concluded that $A_2(C^+)_{CH_3Cl}$ and $A_3(C^+)_{CH_3Br}$ should be allocated to mechanism (l) while $A_2(C^+)_{CH_3Br}$ refers to (k). Hence are obtained the equations

$$A_1(C^+) = I(C) + \Sigma D_4(CH_3X) - D(H_2) \quad (4.12)$$

$$A_2(C^+)_{CH_3Cl} = I(C) + \Sigma D_4(CH_3Cl) \quad (4.13)$$

$$A_2(C^+)_{CH_3Br} = I(C) + \Sigma D_4(CH_3Br) - D(H\text{-}Br) \quad (4.14)$$

$$A_3(C^+)_{CH_3Br} = I(C) + \Sigma D_4(CH_3Br) \quad (4.15)$$

where $\Sigma D_4(CH_3Br) = D(CH_3\text{-}Br) + D(CH_2\text{-}H) + D(CH\text{-}H) + D(C\text{-}H)$

Combiniation of the required data then gives the results set out in Table 15c.

TABLE 15c

	$\Sigma D_4(CH_3X)$ eV.		D(C-H) eV.	
Equns.	X ≡ Cl	X≡Br	X ≡ Cl	X ≡ Br
(4.12)	16.25±0.1	15.65±0.1	3.70±0.25	3.37±0.25
(4.14)	-	15.68±0.1	-	3.4 ±0.25
(4.13)(4.15)	16.23±0.1	15.63±0.1	3.68±0.25	3.35±0.25

As in previous cases, the above values are concordant within the limits of uncertainty and the average D(C-H) = 3.5±0.3 eV. is in good agreement with the estimate of 3.47 eV. as obtained by Herzberg and Gaydon (32) from the spectrum of CH, and also with McDowell and Warren's (31) proposed D(C-H) = 3.6 eV. on the basis of electron impact studies on methane. If $A_1(C^+)$ were assigned to mechanism (h) above, D(C-H) would require to be lowered by an amount

equal to D(H-X) which would result in D(C-H) ≃ 0 . In addition, no reasonable dissociative processes could be chosen to account for $A_2(C^+)$ and $A_3(C^+)$ of CH_3Br, or for $A_2(C^+)$ of CH_3Cl if $A_1(C^+)$ refered to (h) unless widely divergent and improbable values of D(C-H) were assumed. Hence the rejection of (h) is considered to be justified.

If any excess energy is involved in the production of C^+, then the above equations (4.12)-(4.15) must be modified, as in the case of CH^+, to:

$$A(C^+) = I(C) + \Sigma D_4(CH_3X) - D^{(H_2)}_{(HX)} + E \qquad (4.16)$$

$$A(C^+) = I(C) + \Sigma D_4(CH_3X) + E \qquad (4.17)$$

Now $(A_4-A_3)\ (C^+)_{CH_3Cl} = 4.4\pm0.3$ eV., $(A_6-A_5)(C^+)_{CH_3Br} = 3.75\pm0.2$ eV., and $(A_6-A_4)\ (C^+)_{CH_3Br} = 4.5\pm0.2$ eV. The simplest interpretation of these energy differences is that the CH_3X is decomposed to give C^+ according to processes (j), (k), (l) above, but that there is associated with one or more of the fragments, an excess energy E. In Table 16, the observed appearance potentials have been assigned to the appropriate dissociative mechanisms selected on the basis of the above energy differences. Combination of these appearance potentials with the other thermochemical data in equations (4.16) or (4.17) as the case may be yield values of $\Sigma D_4(CH_3X) + E$. Subtraction of the values of $\Sigma D_4(CH_3X)$ calculated on the assumption of no excess energy then gives the amount of surplus energy associated with the particular

dissociation.

TABLE 16

Excess energy associated with the production of C^+ from CH_3X.

App. Pot.	Products	ΣD_4+E eV.	ΣD_4 eV.	E eV.
$A_3(C^+)_{CH_3Cl}$	C^++H_2+H+Cl+E	21.65±0.1	16.25±0.1	5.4±0.2
$A_4(C^+)_{CH_3Cl}$	C^++3H+Cl+E	21.63±0.2	16.25±0.1	5.4±0.3
$A_4(C^+)_{CH_3Br}$	C^++H_2+H+Br+E	21.00±0.1	15.65±0.1	5.35±0.2
$A_5(C^+)_{CH_3Br}$	C^++2H+HBr+E	20.98±0.1	15.65±0.1	5.3 ±0.2
$A_6(C^+)_{CH_3Br}$	C^++3H+Br+E	20.98±0.1	15.65±0.1	5.3 ±0.2

As may be seen, the amount of excess energy is sensibly constant despite the diversity of dissociative processes involved. This suggests that again the energy is electron-:ic rather than kinetic in character, and since only C^+ ions and H atoms are common to all five processes, the electron-:ic excitation must be associated with the C^+ ion. The ground state of C^+ has the electron configuration ($1s^2$, $2s^2$, 2p; ^2P), while the next highest level is the ($1s^2$, 2s, $2p^2$; ^4P) state which lies 5.31 eV. above the ground state (74). Thus the excess energy associated with the production of C^+ from CH_3X is probably accounted for by the transition $C^+(^2P \dashrightarrow {}^4P)$.

The estimated value of E as given above may be verified after the manner described for CH^+. Thus if a value is assumed for L_c and combined with the requisite thermochem-

:ical data in equation (4.18), $\Sigma D_4(CH_3X)$ may be obtained independently of an appearance potential measurement.

$$L_c = \Sigma D_4(CH_3X) - 1\tfrac{1}{2}D(H_2) - \tfrac{1}{2}D(X_2) + \Delta H_f(CH_3X) \quad (4.18)$$

On this basis, taking L_c = 7.386 eV., we obtain $\Sigma D_4(CH_3Cl)$ = 16.26 eV. and $\Sigma D_4(CH_3Br)$ = 15.25 eV., which are in ex-:cellent agreement with the values of $\Sigma D_4(CH_3X)$ obtained in this work. The use of any lower estimate of L_c leads to abnormally high values of $\Sigma D_4(CH_3X)$ which are outwith any observed here. Also the use of a value of $\Sigma D_4(CH_3X)$, calculated on the basis of any other proposed value of L_c, gives results for E which cannot be interpreted in terms of any known state of C^+(or for that part, any of the other fragments produced along with C^+).

For example, suppose L_c = 5.42 eV. (the lowest per-:mitted value), then $\Sigma D_4(CH_3Cl)$ = 18.23 eV., whence E = 3.42 eV. Similarly L_c = 5.89 eV. and 6.13 eV. give values of E = 3.89 eV. and 4.13 eV. respectively. There are, however, no electronic states of C^+ known between 0 and 5.13 eV. Thus the energy would require to be vibrational or translational, which is unlikely when the close similar-:ity of the values of E, obtained on the basis of differing dissociative mechanisms, is considered.

It is therefore concluded that the observations on CH_3Cl and CH_3Br support, with little or no ambiguity, L_c = 7.386 eV.

DISSOCIATIVE PROCESSES IN CH_2X_2(X-Cl,Br).

1. $\underline{CH_2X^+}$: By analogy with previous cases, the most likely way in which this ion is produced is by the mechan-:ism (a) $e^- + CH_2X_2 \longrightarrow CH_2X^+ + X + 2e^-$ (a)

$e^- + CH_2X_2 \longrightarrow CH_2X^+ + X^- + e^-$ (b)

rather than the alternative (b). Hence, assuming that no excess kinetic or electronic energy is present,

$$A(CH_2X^+) = I(CH_2X) + D(CH_2X\text{-}X) \qquad (5.1)$$

where $I(CH_2X)$ is the ionization potential of CH_2X. Sub-:stitution then gives $D(CH_2Cl\text{-}Cl) = 3.2 \pm 0.15$ eV. and $D(CH_2Br\text{-}Br) = 2.6 \pm 0.15$ eV.

If (b) were accepted, then $D(CH_2X\text{-}X)$ would be lowered by an amount equal to the electron affinity of X, which would result in $D(CH_2X\text{-}X) \approx 0$. This implies that the rad-:ical CH_2X is thermodynamically more stable than CH_2X_2 which is absurd, hence (b) is rejected.

2. $\underline{CHCl_2^+}$: The alternative primary dissociation which involves the loss of hydrogen rather than halogen has been observed for CH_2Cl_2. The ion is most probably formed by the process

$$e^- + CH_2Cl_2 \longrightarrow CHCl_2^+ + H + 2e^-$$

whence $A(CHCl_2^+) = I(CHCl_2) + D(CHCl_2\text{-}H)$ (5.2)

which yields $D(CHCl_2\text{-}H) = 3.77 \pm 0.15$ eV.

The other possible mechanism involving H^- instead of H would result in $D(CHCl_2\text{-}H) = 3.03$ eV. No definite choice can be made between these two possible values of $D(CHCl_2\text{-}H)$ since no previous work has been published on this subject; however, in all the cases so far studied, it has been found that mechanisms involving negative ion formation did not yield acceptable values of dissociation energies. Also, no appearance potential of $CHBr_2^+$ could be measured since the realative abundance of the $CHBr_2^+$ ion in the mass spectrum of CH_2Br_2 was too small. This implies that the difference in energy between $D(CH_2Br\text{-}Br)$ and $D(CHBr_2\text{-}H)$ is sufficiently large for CH_2Br^+ to be produced to the almost total exclusion of $CHBr_2^+$. It is further considered that $D(CHBr_2\text{-}H)$ will not be very much different from $D(CHCl_2\text{-}H)$. Now if $D(CHCl_2\text{-}H) = 3.77$ eV., then the energy difference referred to is 1.2 eV. (taking $D(CH_2Br\text{-}Br) = 2.6$ eV.), while if $D(CHCl_2\text{-}H) = 3.03$ eV., then the difference is only 0.4 eV. It is known also that $D(CH_2Cl\text{-}Cl) = 3.2$ eV., and the difference between $D(CH_2Cl\text{-}Cl)$ and $D(CHCl_2\text{-}H)$ is then 0.6 eV. if the higher value of $D(CHCl_2\text{-}H)$ is assumed and 0.2 eV. if the lower value is taken. From this it is seen that since $D(CHCl_2\text{-}H) - D(CH_2Cl\text{-}Cl) \simeq 0.6$ eV. and at the same time both $CHCl_2^+$ and CH_2Cl^+ ions are formed in

approximately equal intensity, it is unlikely that if $D(CHBr_2\text{-}H) - D(CH_2Br\text{-}Br) = 0.4$ eV., $CHBr_2^+$ would have a relative abundance much less than CH_2Br^+. It is concluded therefore that the energy difference $D(CHBr_2\text{-}H) - D(CH_2Br\text{-}Br) = 1.2$ eV., which, on the basis of the assumptions made above, implies that $D(CHCl_2\text{-}H) = 3.77$ eV. is more likely to be the correct one.

3. $\underline{CH_2^+}$: This ion can arise either by loss of a halogen molecule or two halogen atoms according to (c) or (d) respectively:

$$e^- + CH_2X_2 \longrightarrow CH_2^+ + X_2 + 2e^- \qquad (c)$$

$$e^- + CH_2X_2 \longrightarrow CH_2^+ + 2X + 2e^- \qquad (d)$$

Two breaks were observed in the ionization efficiency curves of CH_2^+ for each CH_2X_2. These breaks were separated by 2.45 ± 0.1 eV. and 2.05 ± 0.1 eV. for X ≡ Cl and Br respectively, which correspond closely with $D(Cl_2) = 2.48$ eV. and $D(Br_2) = 1.98$ eV. Hence it is considered that $A_1(CH_2^+)$ refers to (c) and $A_2(CH_2^+)$ to (d). The equations (5.3) and (5.4) can now be applied.

$$A_1(CH_2^+) = I(CH_2) + \Sigma D_2(CH_2X_2) - D(X_2) \qquad (5.3)$$

$$A_2(CH_2^+) = I(CH_2) + \Sigma D_2(CH_2X_2) \qquad (5.4)$$

where $\Sigma D_2(CH_2X_2) = D(CH_2X\text{-}X) + D(CH_2\text{-}X)$. Substitution in (5.3) and (5.4) then gives the results quoted in Table 17a.

TABLE 17a

	$\sum D_2(CH_2X_2)$ eV.		$D(CH_2-X)$ eV.	
Eqn.	X ≡ Cl	X ≡ Br	X ≡ Cl	X ≡ Br
(5.3)	6.68±0.15	5.68±0.15	3.5 ±0.3	3.1 ±0.3
(5.4)	6.65±0.15	5.75±0.15	3.5 ±0.3	3.2 ±0.3

the values of $D(CH_2-X)$ are in good agreement with one another for both X-Cl and Br, and are probably of the correct order of magnitude, i.e. about equal to the corresponding $D(CH_2X-X)$.

The sum $D(CH_2X-X) + D(CH_2-X)$ can be obtained from the equations (5. 5) and (5.6).

$$L_c = \sum D_4(CH_2X_2) - D(H_2) - D(X_2) + \Delta H_f(CH_2X_2) \quad (5.5)$$

where $\sum D_4(CH_2X_2) = D(CH_2X-X) + D(CH_2-X) + D(CH-H) + D(C-H)$ (5.6)

hence $D(CH_2X-X) + D(CH_2-X) = \sum D_4(CH_2X_2) - D(CH-H) - D(C-H)$. If L_c is assumed to be 7.386 eV., D(CH-H) = 5.1±0.3 eV. as stablished above and D(C-H) = 3.47 eV., then $D(CH_2X-X) + D(CH_2-X)$ = 6.7 eV. and 5.7 ±0.3 eV. for X≡Cl and Br respect-:ively. (see below, however, regarding $\Delta H_f(CH_2Br_2)$) These are in fair agreement, considering the margin of un-:certainty with the observed values of $\sum D_2(CH_2X_2)$ This shows that the measured values of $A(CH_2^+)$ are probably correct, and that the values of $D(CH_2X-X)$ and $D(CH_2-X)$ cann-:ot be far from the true values.

The assumption of negative halogen ion formation does not give mutually concordant values of $\sum D_2(CH_2X_2)$ nor are

they in good agreement with the calculated values.

If another value of L_c, e.g. 6.13 eV., is used to calculate $\sum D_2(CH_2X_2)$, this quantity is lowered by 1.2 eV. in each case - which is considered to be outwith the experimental error of our measurements.

4. $\underline{CCl_2^+}$: This ion can arise from CH_2Cl_2 either by loss of H_2 or 2H, i.e. according to:

$$e^- + CH_2Cl_2 \longrightarrow CCl_2^+ + H_2 + 2e^- \qquad (e)$$

$$e^- + CH_2Cl_2 \longrightarrow CCl_2^+ + 2H + 2e^- \qquad (f)$$

Two appearance potentials differing by 4.55±0.2 eV. have been observed for CCl_2^+ and hence A_1 has been assigned to (e) and A_2 to (f). Hence we have:

$$A_1(CCl_2^+) = I(CCl_2) + D(CHCl_2\text{-}H) + D(CCl_2\text{-}H) - D(H_2) \qquad (5.7)$$

$$A_2(CCl_2^+) = I(CCl_2) + D(CHCl_2\text{-}H) + D(CCl_2\text{-}H) \qquad (5.8)$$

Combination of the measured appearance potentials with the other requisite data then gives $D(CCl_2\text{-}H)$ = 3.70±0.35 eV. and 3.73±0.35 eV. by equations (5.7) and (5.8) respectively. This result, in which $D(CCl_2\text{-}H)$ and $D(CHCl_2\text{-}H)$ are approximately equal is reasonable and in keeping with the cases previously discussed.

It is possible, as illustrated in the discussion of CH_2^+ to calculate the value for $D(CHCl_2\text{-}H) + D(CCl_2\text{-}H)$. It has been shown that $\sum D_4(CH_2Cl_2)$ = 15.30 eV. Now since $\sum D_4(CH_2Cl_2)$ is defined as being the total energy required to break the four bonds in CH_2Cl_2 taken in any

order, then, in addition to equation (5.6) we have:

$$\sum D_4(CH_2Cl_2) = D(CHCl_2\text{-}H) + D(CCl_2\text{-}H) + D(CCl\text{-}Cl) + D(C\text{-}Cl) \qquad (5.6b)$$

D(CCl-Cl) = 3.45±0.3 eV. and D(C-Cl) = 4.3 ±0.2 eV. have been obtained in a previous section. Combination of these in (5.6b) gives $D(CCl_2H\text{-}H) + D(CCl_2\text{-}H)$ = 7.6±0.5 eV. this is concordant with the observed value of 7.5±0.2 eV. for this sum and, within the rather large limits of uncertainty, tends to confirm L_c = 7.386 eV.

5. CH^+: Six appearance potentials have been observed for $A(CH^+)$ from CH_2X_2. There are three ways in which CH_2X_2 can decompose under electron bombardment to give unexcited fragments:

$$e^- + CH_2X_2 \longrightarrow CH^+ + HX + X + 2e^- \qquad (g)$$

$$e^- + CH_2X_2 \longrightarrow CH^+ + H + X_2 + 2e^- \qquad (h)$$

$$e^- + CH_2X_2 \longrightarrow CH^+ + H + 2X + 2e^- \qquad (i)$$

It can be shown by consideration of the differences in energy between the various appearance potentials that $A_1(CH^+)$, $A_2(CH^+)$ and $A_4(CH^+)$ for both CH_2X_2 refer to (g), (h) and (i) respectively. It has also been observed from the study of CH_3X that CH^+ can be produced in an excited $^1\Pi$ state 2.99 eV. above the ground $^1\Sigma^+$ state. This is also found to be true for CH_2X_2 since $A_3(CH^+)$, $A_5(CH^+)$ and $A_6(CH^+)$ can be correlated with dissociative processes analogous to (g),(h) and (i) but in which a constant energy increment of ~3 eV. appears. These are denoted (g'), (h')

and (i').

$$e^- + CH_2X_2 \longrightarrow CH^+(^1\Pi) + HX + X + 2e^- \quad (g')$$

$$e^- + CH_2X_2 \longrightarrow CH^+(^1\Pi) + H + X_2 + 2e^- \quad (h')$$

$$e^- + CH_2X_2 \longrightarrow CH^+(^1\Pi) + H + 2X + 2e^- \quad (i')$$

The above six decomposition paths lead to equations (5.9) - - - (5.11')

$$A_1(CH^+) = F - D(H-X) \quad (5.9)$$

$$A_2(CH^+) = F - D(X_2) \quad (5.10)$$

$$A_3(CH^+) = F - D(H-X)+E \quad (5.9')$$

$$A_4(CH^+) = F \quad (5.11)$$

$$A_5(CH^+) = F - D(X_2) + E \quad (5.10')$$

$$A_6(CH^+) = F + E \quad (5.11')$$

where $F = I(CH) + \sum D_3(CH_2X_2)$ and $E = 2.99$ eV. denotes the energy of the transition $CH^+(X.^1\Sigma^+) \longrightarrow CH^+(A.^1\Pi)$. In Table 17b the required data have been combined in the appropriate equation to give the corresponding values of $\sum D_3(CH_2X_2) = D(CH_2X-X) + D(CH_2-X) + D(CH-H)$ and $D(CH-H)$.

TABLE 17b

	$\sum D_3(CH_2X_2)$ eV.		D(CH-H) eV.	
Equn.	X ≡ Cl	X ≡ Br	X ≡ Cl	X ≡ Br
(5.9)	11.82±0.1	10.87±0.1	5.15±0.25	5.15±0.25
(5.10)	11.72±0.1	10.75±0.1	5.05±0.25	5.03±0.25
(5.11)	11.77±0.15	10.87±0.15	5.1 ±0.3	5.16±0.3
(5.9')	11.83±0.15	10.78±0.1	5.15±0.3	5.06±0.25
(5.10')	11.91±0.15	10.76±0.15	5.25±0.3	5.04±0.3
(5.11')	11.78±0.15	10.78±0.15	5.1 ±0.3	5.06±0.3

The average value of D(CH-H) = 5.15±0.3 eV. is in good agreement with that deduced from studies on CH_3X.

It is easily shown that:

$$\Sigma D_3(CH_2X_2) = \Sigma D_4(CH_2X_2) - D(C\text{-}H)$$

$\Sigma D_4(CH_2X_2)$ may be calculated assuming a value for L_c (equn. (5.5)) whence subtraction of D(C-H) = 3.47 eV. gives $\Sigma D_3(CH_2X_2)$. The value calculated for $\Sigma D_3(CH_2Cl_2)$ by this procedure is 11.83 eV. which is in excellent agreement with the average "observed" value of 11.8 ±0.2 eV. Similarly $\Sigma D_3(CH_2Br_2)$ becomes 10.82 eV. if $\Delta H_f(CH_2Br_2)$ = -0.4 eV. is assumed. Cottrell (5c) has however pointed out that this heat of formation is a "calculated" value and not a purely experimental quantity. Thus less reliance must be placed on $\Sigma D_3(CH_2Br_2)$ derived from $\Delta H_f(CH_2Br_2)$ than on the corresponding quantity for CH_2Cl_2.

6. $\underline{C^+}$: There are a large number of ways in which CH_2X_2 may dissociate to produce C^+. The simplest mechanism - that producing monoatomic fragments in their ground state, is (j):

$$e^- + CH_2X_2 \longrightarrow C^+ + 2H + 2X + 2e^- \qquad (j)$$

It is considered that of the six appearance potentials observed for $A(C^+)_{CH_2Cl_2}$, A_3 refers to (j), whence:

$$A(C^+) = I(C) + \Sigma D_4(CH_2X_2) \qquad (5.12)$$

Substitution of $A_3(C^+)_{CH_2Cl_2}$ gives D(C-H) = 3.5 ±0.3 eV. in good agreement with the spectroscopic value of 3.47 eV.

Examination of the energy differences between A_1, A_2 and $A_3(C^+)$ from CH_2Cl_2 shows that $A_1(C^+)$ and $A_2(C^+)$ refer to processes (k) and (l) respectively.

$$e^- + CH_2X_2 \longrightarrow C^+ + H_2 + 2X + 2e^- \qquad (k)$$

$$e^- + CH_2X_2 \longrightarrow C^+ + 2H + X_2 + 2e^- \qquad (l)$$

leading to equations (5.13) and (5.14)

$A(C^+) = G-D(H_2)$ (5.13) and $A(C^+) = G-D(X_2)$ (5.14)

where $G = \sum D_4(CH_2X_2) + I(C)$. No appearance potential corresponding to (m) was observed for CH_2Cl_2.

$$e^- + CH_2X_2 \longrightarrow C^+ + HX + H + X + 2e^- \qquad (m)$$

The reason for this is probably that the required break in the ionization efficiency curve of C^+ would differ from A_1 by only 0.1 eV. Such a small difference could not be resolved by the technique used. However, in the case of CH_2Br_2, the difference amounts to about 0.8 eV. and as may be seen (Table 17d), process (m) is represented.

The alternative modes of decomposition (n) and (o) must be rejected, since the use of these mechanisms gives abnormally low and widely discordant values for D(C-H).

$$e^- + CH_2X_2 \longrightarrow C^+ + H_2 + X_2 \qquad (n)$$

$$e^- + CH_2X_2 \longrightarrow C^+ + 2HX \qquad (o)$$

The remaining values of $A(C^+)$ of CH_2Cl_2 can be interpreted in terms of (j'), (k') and (l') which are identical with (j), (k), and (l) except that C^+ is produced in its first excited ^4P state rather than its ground ^2P state. Hence we may construct the equations:

$$A(C^+) = G + K \qquad (5.12')$$

$$A(C^+) = G - D(H_2) + K \qquad (5.13')$$

$$A(C^+) = G - D(X_2) + K \qquad (5.14')$$

where G is as defined above and K = 5.13 eV. is the energy of the transition $C^+(^2P \longrightarrow {}^4P)$.

By similar arguments, the eight appearance potentials of C^+ from CH_2Br_2 can be interpreted in terms of (j), (k), (l), (m), (j'), (k'), (l'), and (m'):

$$e^- + CH_2X_2 \longrightarrow C^+(^4P) + HX + H + X + 2e^- \qquad (m')$$

The equations corresponding to (m) and (m') are:

$A(C^+) = G-D(H-X)$ (5.15) $A(C^+) = G-D(H-X) + K$ (5.15')

In Tables 17c and 17d are listed the values of $\Sigma D_4(CH_2X_2)$ and D(C-H) obtained from the observed appearance potentials according to the equations appropriate for the dissociative process to which each refers.

TABLE 17c

$\Sigma D_4(CH_2Cl_2)$ and D(C-H) from $A(C^+)_{CH_2Cl_2}$.

$A(C^+)$	Products	Equn.	$\Sigma D_4(CH_2Cl_2)$ eV.	D(C-H) eV.
A_1	$C^+(^2P) + H_2 + 2X$	(5.12)	15.25±0.15	3.55±0.25
A_2	$C^+(^2P) + 2H + X_2$	(5.13)	15.26±0.15	3.45±0.25
A_3	$C^+(^2P) + 2H + 2X$	(5.14)	15.28±0.1	3.5 ±0.3
A_4	$C^+(^4P) + H_2 + 2X$	(5.12')	15.57±0.2	3.8 ±0.4
A_5	$C^+(^4P) + 2H + X_2$	(5.13')	15.48±0.2	3.7 ±0.4
A_6	$C^+(^4P) + 2H + 2X$	(5.14')	15.50±0.2	3.7 ±0.4

TABLE 17d

$\Sigma D_4(CH_2Br_2)$ and D(C-H) from $A(C^+)_{CH_2Br_2}$.

$A(C^+)$	Products	Equn.	$\Sigma D_4(CH_2Br_2)$ eV.	D(CH) eV.
A_1	$C^+(^2P) + H_2 + 2X$	(5.12)	14.25±0.05	3.45±0.25
A_2	$C^+(^2P) + HX + H + X$	(5.15)	14.48±0.1	3.7 ±0.3
A_3	$C^+(^2P) + 2H + X_2$	(5.13)	14.21±0.1	3.4 ±0.3
A_4	$C^+(^2P) + 2H + 2X$	(5.14)	14.23±0.1	3.4 ±0.3
A_5	$C^+(^4P) + H_2 + 2X$	(5.12')	14.52±0.2	3.7 ±0.4
A_6	$C^+(^4P) + HX + X + H$	(5.15')	14.50±0.2	3.7 ±0.4
A_7	$C^+(^4P) + 2H + X_2$	(5.13')	14.43±0.2	3.6 ±0.4
A_8	$C^+(^4P) + 2H + 2X$	(5.14')	14.40±0.2	3.6 ±0.4

The values of D(C-H) obtained are in good agreement with the spectroscopically preferred estimate of 3.47 eV. which indicates that the dissociative processes selected are probably correct. The average observed $\Sigma D_4(CH_2Cl_2)$ = 15.4 ±0.3 eV. is concordant with $\Sigma D_4(CH_2Cl_2)$ = 15.30 eV. calculated from L_c = 7.386 eV. Consideration of any of the lower estimates of L_c gives calculated values of $\Sigma D_4(CH_2Cl_2)$ appreciably outwith the limits of uncertainty of the above measurements; e.g. L_c = 6.13 eV. gives ΣD_4 = 14.04 eV.

Similarly, combiniation of L_c = 7.386 eV. gives $\Sigma D_4(CH_2Br_2)$ =14.29 eV. taking ΔH_f (CH_2Br_2) = -0.4 eV. Although this is in reasonable agreement with the measured $\Sigma D_4(CH_2Br_2)$ =14.4±0.4 eV., it must be remembered that

$\Delta H_f(CH_2Br_2)$ has not been experimentally established, and that the results from CH_2Br_2 should not be used to strictly confirm L_c = 7.386 eV. However, there is a clear indication from the results of the investigations of CH_3X and CH_2Cl_2 that L_c does in fact = 7.386 eV. Hence $\Delta H_f(CH_2Br_2)$ = -0.4 eV. is probably correct, but the uncertainties in the experimental measurements are too large to allow of a reasonably precise estimate of this quantity.

DISSOCIATIVE PROCESSES IN CHX_3 (X ≡ Cl, Br)

1. CHX_2^+: By analogy with the other compounds discussed above, CHX_2^+ probably arises by loss of a halogen atom: $e^- + CHX_3 \longrightarrow CHX_2^+ + X + 2e^-$ (a) whence

$$A(CHX_2^+) = I(CHX_2) + D(CHX_2\text{-}X) \qquad (6.1)$$

Substitution in (6.1) gives $D(CHCl_2\text{-}Cl) = 2.9 \pm 0.15$ eV. and $D(CHBr_2\text{-}Br) = 2.65 \pm 0.15$ eV. For similar reasons to those previously given, mechanisms involving negative ion formation are rejected for the production of this and all subsequent ions derived from CHX_3. Semeluk and Bernstein (75) have estimated $D(CHCl_2\text{-}Cl) \simeq 3.1$ eV. from a study of the thermal decomposition of chloroform. This result is in fair agreement with the value proposed here.

2. CHX^+: This ion may arise either by loss of a halogen molecule or two halogen atoms. Both types of process have been observed, corresponding to (b) and (c):

$$e^- + CHX_3 \longrightarrow CHX^+ + X_2 + 2e^- \qquad (b)$$

$$e^- + CHX_3 \longrightarrow CHX^+ + 2X + 2e^- \qquad (c)$$

from which may be deduced equations (6.2) and (6.3)

$$(b) \sim A_1(CHX^+) = I(CHX) + \Sigma D_2(CHX_3) - D(X_2) \qquad (6.2)$$

$$(c) \sim A_2(CHX^+) = I(CHX) + \Sigma D_2(CHX_3) \qquad (6.3)$$

where $\Sigma D_2(CHX_3) = D(CHX_2\text{-}X) + D(CHX\text{-}X)$. The results are

summarized in table 18a.

TABLE 18a

$\Sigma D_2(CHX_3)$ and D(CHX-X) from $A(CHX^+)$.

	$\Sigma D_2(CHX_3)$ eV.		D(CHX-X) eV.	
Equn.	X ≡ Cl	X ≡ Br	X ≡ Cl	X ≡ Br
(6.2)	6.40±0.15	5.25±0.15	3.5±0.3	2.6±0.3
(6.3)	6.35±0.15	5.22±0.15	3.5±0.3	2.6±0.3

These results, in which $D(CHX_2-X)$ and D(CHX-X) are approx-:imately equal, are in keeping with those observations already noted for the other series; hence the decomposit-:ion paths selected for each appearance potential are likely to be correct.

3. CCl_2^+: The most favoured modes of formation of CCl_2^+ are by (d) or (e):

$$e^- + CHCl_3 \longrightarrow CCl_2^+ + HCl + 2e^- \qquad (d)$$

$$e^- + CHCl_3 \longrightarrow CCl_2^+ + H + Cl + 2e^- \qquad (e)$$

from which may be obtained the equations:

$$(d) \sim A_1(CCl_2^+) = I(CCl_2) + D(CCl_2H-Cl) + D(CCl_2-H) - D(Cl_2) \qquad (6.4)$$

or $$(d) \sim A_1(CCl_2^+) = I(CCl_2) + D(CCl_3-H) + D(CCl_2-Cl) - D(Cl_2) \qquad (6.5)$$

$$(e) \sim A_2(CCl_2^+) = I(CCl_2) + D(CCl_2H-Cl) + D(CCl_2-H) \qquad (6.6)$$

or $$(e) \sim A_2(CCl_2^+) = I(CCl_2) + D(CCl_3-H) + D(CCl_2-Cl) \qquad (6.7)$$

Combination of the measured appearance potentials with $I(CCl_2)$ = 13.1±0.1 eV. obtained in a previous section, $D(CCl_3-H) + D(CCl_2-Cl)$ = 6.65±0.2 eV. is deduced using (6.5) and 6.7 ±0.2 eV. by (6.7). $D(CCl_3-H)$ = 3.90 eV.

has been measured by Szwarc (114), hence $D(CCl_2-Cl) = 2.75 \pm 0.2$ eV. and 2.8 ± 0.2 eV. by (6.5) and (6.7) respectively. This is in fair agreement with $D(CCl_2-Cl) = 2.4 \pm 0.3$ eV. estimated from the electron impact studies on CCl_4 which indicated that the measured appearance potentials are of the correct order of magnitude and establishes the validity of the selected dissociative mechanisms.

Considering now equations (6.4) and (6.6), we have $D(CHCl_2-Cl) + D(CCl_2-H) = 6.65 \pm 0.2$ eV. and 6.7 ± 0.2 eV. respectively. Subtraction of $D(CHCl_2-Cl) = 2.9 \pm 0.15$ eV. obtained above, gives an average $D(CCl_2-H) = 3.8 \pm 0.35$ eV. The relative intensity of CCl_3^+ in the mass spectrum of $CHCl_3$ is weak, hence $D(CCl_3-H)$ could not be measured. This is not surprising since $D(CHCl_2-Cl) = 2.9$ eV. and $D(CCl_3-H) = 3.9$ eV. The difference in energy of 1 eV. would be ample to ensure that the initial dissociation consisted almost exclusively of halogen rather than hydrogen loss, which would result in the low relative abundance of CCl_3^+. On the other hand, since $D(CHCl-Cl) = 3.5$ eV. and $D(CCl_2-H) = 3.75$ eV., the difference between the two bond energies is much smaller and the probability of the second dissociation involving rupture of a carbon - halogen bond would be about equal to that consisting of carbon - hydrogen fission. This causes CCl_2^+ to be present in appreciably greater concentration in the mass spectrum than CCl_3^+.

4. CH^+: From a consideration of the various ways in which CH^+ has been produced from CH_3X and CH_2X_2, we would expect in the present instance that CH^+ would be formed by one or more of the mechanisms (f) - - - (g') :

$$e^- + CHX_3 \text{ ---- } CH^+(^1\Sigma^+) + X_2 + X + 2e^- \qquad (f)$$

$$e^- + CHX_3 \text{ ---- } CH^+(^1\Sigma^+) + 3X + 2e^- \qquad (g)$$

$$e^- + CHX_3 \text{ ---- } CH^+(^1\Pi) + X_2 + X + 2e^- \qquad (f')$$

$$e^- + CHX_3 \text{ ---- } CH^+(^1\Pi) + 3X + 2e^- \qquad (g')$$

In fact, for both CHX_3, appearance potentials corresponding to all four of these processes have been observed. By similar arguments to those given for the two previous series, those appearance potentials A_1 - - - A_4 have been assigned to equations (6.8) - - - (6.9').

(f) ~ $A_1(CH^+)=F-D(X_2)$(6.8): (g) ~ $A_2(CH^+)=F$ (6.9)

(f')~ $A_3(CH^+)=F+E-D(X_2)$,(6.8'): (g')~$A_4(CH^+)=F+E$ (6.9')

where $F = I(CH) + \Sigma D_3(CHX_3)$; $\Sigma D_3(CHX_3) = D(CHX_2-X) + D(CHX-X) + D(CH-X)$ and E = 2.99 eV. is the energy of the transition $CH^+(X.^1\Sigma^+) \rightarrow (A.^1\Pi)$. The values of $\Sigma D_3(CHX_3)$ and D(CH-X) obtained by this procedure are given in Table 18b.

TABLE 18b

	$\Sigma D_3(CHX_3)$ eV.		D(CH - X) eV.	
Equn.	X ≡ Cl	X ≡ Br	X ≡ Cl	X ≡ Br
(6.8)	11.00±0.1	9.55±0.15	4.6±0.25	4.3±0.3
(6.9)	10.82±0.15	9.47±0.15	4.5±0.3	4.25±0.3
(6.8')	11.06±0.15	9.61±0.15	4.7±0.3	4.35±0.3
(6.9')	10.83±0.15	9.58±0.15	4.5±0.3	4.35±0.3

It can be seen that the values of D(CH-X) are in reasonable agreement with one another. Consideration of the series D(CH-H) = 5.1 eV., D(CH-Cl) = 4.6 eV. and D(CH-Br) = 4.3 eV. shows that there is a progressive lowering of bond energy as hydrogen is replaced by halogen. Similar trends are noted in the series $D(CH_3-H)$ = 4.12 eV. (31) $D(CH_3-Cl)$ = 3.40 eV. and $D(CH_3-Br)$ = 2.33 eV. and also $D(CH_2-H)$ = 4.15 eV., $D(CH_2-Cl)$ = 3.5 eV. and $D(CH_2-Br)$ = 3.1 eV. This shows that the results obtained above are consistent with previous observation and consequently that they are of the correct order of magnitude.

The value of $\Sigma D_3(CHCl_3)$ calculated from $\Delta H_f(CHCl_3)$ on the assumption that L_c = 7.386 eV. is 10.96 eV. which correlates well with the average measured $\Sigma D_3(CHCl_3)$ = 10.9 $\pm$0.2 eV. The use of any lower estimate of L_c gives a calculated $\Sigma D_3(CHCl_3)$ which is considerably outwith the limits of accuracy of the measured value. A similar procedure may be followed to evaluate $\Sigma D_3(CHBr_3)$ but, as in the case of CH_2Br_2, $\Delta H_f(CHBr_3)$ has not been measured and the figure, - 0.4 eV., quoted in the literature is a "calculated" value. However, taking L_c = 7.386 eV. together with the above value for $\Delta H_f(CHBr_3)$, $\Sigma D_3(CHBr_3)$ may be estimated to be 9.46 eV., with which the average measured quantity, 9.5$\pm$0.2 eV., is reasonably consistent.

5. C^+: Examination of the appearance potentials of

C^+ from CHX_3 indicate that they may be correlated with the six dissociative processes (h) - - (j') given:

$$e^- + CHX_3 \longrightarrow C^+(^2P) + HX + 2X + 2e^- \qquad (h)$$

$$e^- + CHX_3 \longrightarrow C^+(^2P) + H + X + X_2 + 2e^- \qquad (i)$$

$$e^- + CHX_3 \longrightarrow C^+(^2P) + H + 3X + 2e^- \qquad (j)$$

(h'), (i') and (j') are identical with (h), (i) and (j) except that C^+ is produced in an excited ^4P state instead of the ground ^2P level. From these modes of decomposition, equations (6.10), - - - (6.12') may be derived.

$$(h) \sim A(C^+) = G - D(H-X) \qquad (6.10)$$

$$(i) \sim A(C^+) = G - D(X_2) \qquad (6.11)$$

$$(j) \sim A(C^+) = G \qquad (6.12)$$

where $G = I(C) + \sum D_4(CHX_3)$, and $\sum D_4(CHX_3) = D(CHX_2-X) + D(CHX-X) + D(CH-X) + D(C-H)$. (j'), (i') and (h') ~ (6.12') (6.11') and (6.10') respectively. These equations are identical with the corresponding "unprimed" equations except that 5.13 eV. (the energy of the transition C^+ (^2P --^4P)) has been added to the R.H.S. of each. In Tables 18c and 18d the observed appearance potentials have been assigned to their appropriate dissociation mechanism, while from the corresponding equation, $\sum D_4(CHX_3)$ and D(C-H) have been calculated.

TABLE 18c

App. Pot. eV.	Mech.	Equn.	$\sum D_4(CHCl_3)$ eV.	D(C-H) eV.
23.15±0.05	(i)	(6.11)	14.36±0.05	3.5±0.3
25.76±0.05	(j)	(6.12)	14.49±0.05	3.6±0.3
27.9 ±0.1	(i')	(6.11')	14.38±0.1	3.5±0.4
30.8± 0.1	(j')	(6.12')	14.40±0.1	3.5±0.4

TABLE 18d

App. Pot. eV.	Mech.	Equn.	$\Sigma D_4(CHBr_3)$ eV.	D(C-H) eV.
20.50±0.05	(h)	(6.10)	12.98±0.05	3.4±0.25
22.25±0.05	(i)	(6.11)	12.96±0.05	3.4±0.25
24.30±0.05	(j)	(6.12)	13.03±0.05	3.5±0.25
25.8 ±0.1	(h')	(6.10')	13.15±0.1	3.6±0.3
27.55±0.1	(i')	(6.11')	13.13±0.1	3.6±0.3
29.55±0.1	(j')	(6.12')	13.15±0.1	3.6±0.3

Once again, the values of D(C-H) are in good agreement with those values estimated in previous sections and also with the spectroscopic D(C-H) = 3.47 eV. (3,2). The average $\Sigma D_4(CHCl_3)$ =14.4±0.2 eV. correlates well with the heat of atomization of chloroform = 14.43 eV. calculated on the basis of L_c = 7.386 eV. and $\Delta H_f(CHCl_3)$ = -1.04 eV. The experimental error in the determination of $\Sigma D_4(CHCl_3)$ does not permit consideration of any lower value of L_c. The use of the "calculated" $\Delta H_f(CHBr_3)$ = -0.4 eV. gives $\Sigma D_4(CHBr_3)$ = 12.93 eV. with which the average measured value of 13.1±0.2 eV. may be compared.

CONCLUSION.

From a consideration of the bond energies measured in the foregoing sections, it will be apparent that they form a reasonably self-consistent set and, where appropriate, are equal to one another within the limits of experimental accuracy. Also, these values are in good agreement with those which have been published in the literature. From this, it is concluded that all the dissociative mechanisms chosen are the correct ones. This is especially true in the cases where several appearance potentials have been ob-:served for a particular ion, because there is a much greater probability of the establishment of a unique patt-:ern of dissociation where, say, six appearance potentials are distinguishable than where only one or two can be meas-:ured. In addition, as in the case of CX_4 ($X \equiv F, Cl, Br,$) given above, unity has been preserved in the nature of the dissociative processes chosen; i.e. no special mode of decomposition of questionably validity has had to be post-:ulated to explain any particular appearance potential.

From the results, values of $\Sigma D_n(R)$ ($n=2,3,4$; $R \equiv CH_3X$, CH_2X_2, CHX_3; $X \equiv Cl$, Br) were deduced at each stage. The close correlation between them and the corresponding values of $\Sigma D_n(R)$ calculated on the basis of L_c = 7.386 eV. shows that this value for the latent heat of carbon is the most likely. The assumption of any other estimate of L_c

gives values of $\Sigma D_n(R)$ which are well outwith the limits of accuracy of those obtained from the measured appearance potentials. The only way in which the observed results could be reconciled with a lower value of L_c is by the assumption of a completely different set of dissociative mechanisms. This would not give such good correlation among the bond energies.

It is, therefore, concluded that the results of these studies are compatible only with $L_c = 7.386$ eV.

by Eyring and his co-workers (76), postulates that the initial effect of electron bombardment on a molecule is produce the excited molecular ion which remains intact while the excitation energy is being randomly distributed among the internal degrees of freedom. This parent ion then undergoes unimolecular decomposition into various product ions which can then dissociate further unimolecu

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SECTION 2.

The Mass Spectra of Camphor and Some of its Halogen Derivatives.

Introduction:

Although several attempts have been made to discover common features in the mass spectra of different types of molecules, the extreme variability of the "cracking patterns" even of molecules of very similar structure types has prevented the formulation of any general rules controlling the decomposition of molecules by electron impact. The position is critically reviewed by Field and Franklin (4) and Beynon (110). Only a brief account of the position as regards polyatomic molecules will be given here

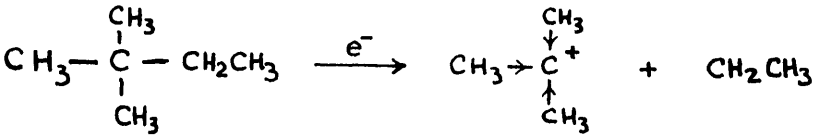
The statistical theory of mass spectra, as proposed by Eyring and his co-workers (76), postulates that the initial effect of electron bombardment on a molecule is to produce the excited molecular ion which remains intact while the excitation energy is being randomly distributed among its internal degrees of freedom. This parent ion then undefgoes unimolecular decomposition into various product ions which can then dissociate further unimolecularly. Mass spectra may be predicted by thistheory, but since the associated mathematics are quite complex, it is not well suited for practical application, except to relatively simple molecules such as propane.

The paraffin hydro-carbons have been the most extensively investigated with a view to the discovery of any unifying principles which could apply to the homologous series. The normal paraffins have been studied by Viallard and Magat (77) who found that the intensities of the parent molecule ions decreased with increasing chain length. These observations were extended to the high molecular weight region (up to M.W. of about 600) by O'Neal and Wier (78) who estimated that for the compound $C_{42}H_{86}$ the parent ion would no longer be detectible. This behavious implies that as the size of the molecule increases, the number of ways in which the parent ion can further dissociate becomes so large that finally, in the time taken for an ion to traverse the mass spectrometer tube from ion source to collector, all the initially formed parent ions have decomposed into smaller fragments.

Furthermore, it was noted in the above experiments that fragment ions which possessed an odd mass number e.g. $C_3H_5^+$, $C_3H_7^+$, $C_4H_9^+$ etc. occurred in higher relative abundance than ions of even number. This may be correlated with the observation of Friedman and Long (79) that ions which have an even number of electrons are, in general, more stable than those having an odd number.

The effect of chain branching has been investigated by Mohler and his collaborators (80) for the cases of the isomeric octanes and nonanes.[73] The most obvious effect

which is made manifest by chain branching is the marked reduction in the relative intensity of the parent ion. This is especially true for a molecule containing a quaternary carbon atom. (e.g. 2: 2 dimethyl butane) The reason for this behaviour probably lies in the fact that a compound containing a quaternary centre can give rise to a tertiary carbonium ion. Taking the example above:



It is well known from studies of the rates of solvolysis of alkyl halides (81) that a tertiary carbonium ion is much more readily produced than the primary ion $R\text{-}CH_2^+$, say. In a tertiary ion, the inductive effect of the alkyl groups is to repel electrons onto the positively charged centre and hence partly compensate for the electron deficiency in the central carbon atom. This means that the activation energy of the decomposition reactions of the parent ion will be so low that most of them will have undergone further dissociation before they reach the collector.

Similar considerations may be applied to molecules containing tertiary carbon centres (e.g. isobutane). However, in this case a secondary carbonium ion is obtained. Such an ion hasan appreciably higher energy than a tertiary ion and hence fewer parent ions would decompose before reaching the collector than would be the case if a tertiary carbonium ion could be formed.

Some mono-olefins have been studied by Brown and Gill-:iams (82). They have pointed out that these compounds tend to rupture at the C-C bond which is located β-to the double bond, giving an allyl type fragment. Reed (83) has also shown that allylic bond fission occurs in the electron impact induced dissociation of cholestane, ergo-:stane and lanost-9:11-ene. The same author has, how-:ever, shown (84) that in the case of β-amyrin, the allylic bond fission reaction is subordinate to the pro-:gressive aromatization of the alicyclic rings in the mole-:cule. This has been further confirmed by Reed and Gil-:christ (85) who examined the spectra of α-pinene, camphene and nor-camphor. Here also was marked evidence that the monoterpenes had undergone dissociation in such a way as to produce an aromatic system. This phenomenon is now thought to be fairly common in an alicyclic system which possesses a C-C or C-O double bond. It will be shown be-:low that camphor and its halogen derivitives can also de-:compose this way. On the other hand camphane and nor-:camphane (85) gave very little evidence of aromatization, straightforward dissociation into acyclic fragments being predominant.

A series of alkyl benzenes have been investigated by Kinney and Cook (86) and Meyerson (34) who observed that these compounds had a much greater tendancy to form benzyl type ions rather than phenyl type. This is in accordance

with the thermochemistry of the two systems. Thus $\Delta H_f(C_6H_5^+)$ = 12.9 eV. while $\Delta H_f(C_7H_7^+)$= 9.5-10 eV. and while measurements of the actual energies of alkyl substit-:uted phenyl ions are hampered by the occurrence of facile rearrangement to a benzyl type ion, it is unlikely that alkyl substitution would affect the difference between the heats of formation of the two types of ion. It has been postulated by Meyerson and Rylander (87) that the $C_7H_7^+$ ion is a tropylium rather than a benzyl ion (see further in section 3 below).

A preliminary investigation of the mass spectra of some condensed polynuclear aromatic hydrocarbons has been carried out by Reed and Snedden (88) who observed that the ion of greatest intensity corresponds with the parent molecule (P = 100%). The remainder of the spectrum consists of fragment ions of low ($\sim$ 1%) relative abundance with the exception of the following fairly prominent ones, P-1 $\simeq$ 7%, P-2 $\simeq$ 20%, P-26 $\simeq$ 2% and the doubly charged parent ion, $\frac{1}{2}$P= 10-25% these being approximate values. Some theoretical studies have been made by Lester (89) on the "cracking pat-:terns" of certain aromatic hydrocarbons. The results suggest that the presence of the ion P-26 corresponds to the elision of CH$\equiv$CH from the parent molecule.

Probably the greatest drawback to the unequivocal ass-:ignment of molecular structure from the examination of a

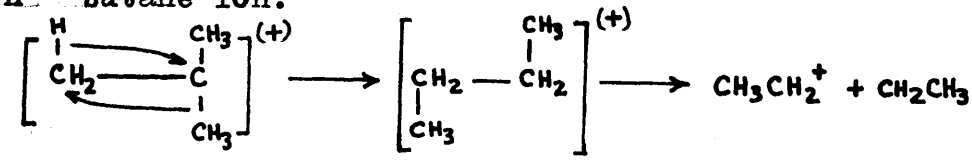
mass spectrum is the possibility of rearrangement of an ion during its formation; i.e. ionic fragments are found in the mass spectrum which cannot be formed by simple cleavage of one or more bonds in the molecule. The smallest paraffin hydrocarbon which unequivocally undergoes a rearrangement decomposition is isobutane which gives rise to $C_2H_5^+$ ions with an intensity of about 6% of the largest peak in the spectrum. Examination of a large number of spectra shows that rearrangements are very common and, while in most cases rearrangement peaks are small (~10%), some compounds are encountered (e.g. 2:2 dimethyl butane) in which the most intense peak in the spectrum corresponds to a rearrangement processes.

The question of the general mechanisms by which rearrangements might occur has been discussed in some detail by both Langer (90) and McLafferty (91). Field and Franklin (4) have also given a critical review of the subject. Langer has considered three possible mechanisms.

(a) <u>The Skeletal Isomerization Theory</u>.

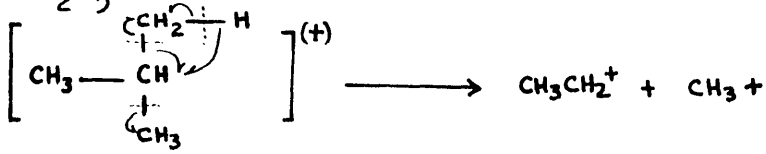
Under the influence of the electron bombardment, but before the occurrence of any dissociation, the molecule ion undergoes isomerization to some other structure which then fragments at its chemical bonds in the normal fashion to give the rearranged ion. For example, it is proposed that the isobutane ion first rearranges partly, at least,

to the n- butane ion.



(b) The Electron Migration Theory.

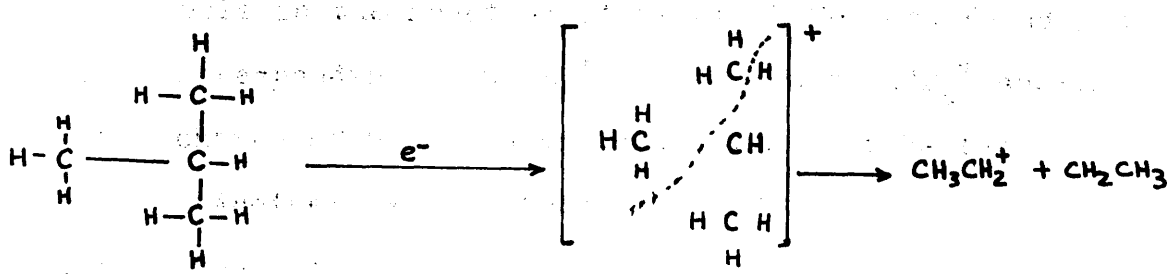
This is simply a process whereby the bonding electrons are shifted from one atom or atomic group to another. There is the possibility that only those associated with hydrogen atoms are involved resulting in an apparent free-:migration of hydrogen atoms in the molecule but, on the other hand, the whole or part of the carbon skeleton may also part. Langer represents the process for the product-:ion of $C_2H_5^+$ from isobutane as:



It can be assumed that at the instant of dissociation a hydrogen atom is acquired from the surrounding hydrogen cloud by the central carbon atom. The drawback, however, to the application of the Electron Migration Theory to this particular process is that the appearance potential of $C_2H_5^+$ indicates that the neutral fragment obtained is the C_2H_5 radical rather than CH_3 and CH_2.(92)

(c) The Randomization Theory.

The essence of this hypothesis isthat, as a result of the electon bombardment, all directed bonds in the molecule vanish and regrouping occurs statisically. For emample:



It is considered that this latter theory is much less likely than the other two (4) for the following reasons:

(1) The energy required to cause homolytic fission of an appreciable number of bonds in a polyatomic molecule is considerably greater than that which seems to be imparted by the bombarding electron.

(2) Such a mechanism would not appear to account for the dependence of the mass spectra of isomeric molecules on molecular structure.

McLafferty has classified rearrangement phenomena under the headings of "Random" and "Specific" rearrangements.

" Random" rearrangements are characterized by a random general exchange of atoms in the newly formed molecule ion. Since there is usually little difference in energy between the various atomic arrangements produced, no particular ionic species is especially favoured over the other possible structures and as a result, a family of rearrangement ions of relatively low intensity are often produced. Rearrangement fragments of this sort are often observed in the mass spectra of partially deuterated hydrocarbons.

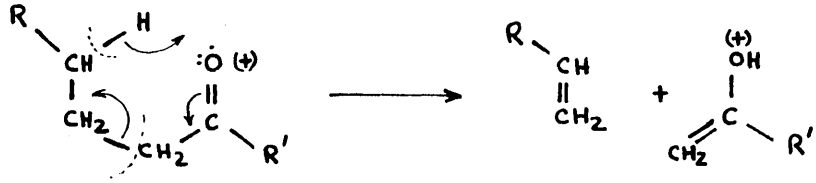
For example in the spectrum of $CD_3CD_2CD_2CH_3$ are found (93) peaks corresponding to $C_3HD_6^+$, $C_3H_2D_5^+$ and $C_2HD_4^+$ showing that exchange of hydrogen and deuterium must be taking place. Another example (94) is C_6H_5OD where the presence of such ions as C_3D^+ demonstrate that the deuterium atom is free to migrate, to some extent at least, into the aromatic nucleus. This behaviour is not confined to hydrogen atoms. Rearrangement ions have been obtained in analogous fashions from perhalocarbons due to migration of bromine atoms, (91), while C_2^+ and C_2H^+ ions have been ob-:tained in the spectrum of s-triazene (95).

The "Specific" type of rearrangement is usually assoc-:iated with the strong directing influence of some polar or other functional group in the molecule. Alternatively, the production of a sterically favoured intermediate or the formation of an unstable fragment from a straightforward bond cleavage can result in such a rearrangement. Many examples of this type can be regarded as a dissociation in which the neutral portion split off from the original ion is replaced by a smaller fragment of that neutral radical (96). A prominent factor in most "specific" rearrange-:ments seems to be the stabilities of the products. Since molecular bonding invdves electron pairs, molecules and the more stable ions have an even number of electrons, while the less stable ions and free radicals usually have an odd number. On this basis, McLafferty (91) has further

classified these isomerizations according to whether the initially formed ion and its decomposition products con-:tain an odd or even number of electrons. In may case, it is found that the initially formed ion (having an odd number of electrons) decomposes into an olefin and a smaller ion (still with an odd number of electrons but having less energy than the parent). An example of this is the migration of hydrogen on rupture of a bond β- to an electron withdrawing group ($>CO$, -CN etc.) (97-102).

$$(R'CO\text{-}CH_2\text{-}CH_2\text{-}CH_2R)^+ \longrightarrow (R'COCH_3)^+ + RCH{=}CH_2.$$

A possible general mechanism has been given by McLafferty:



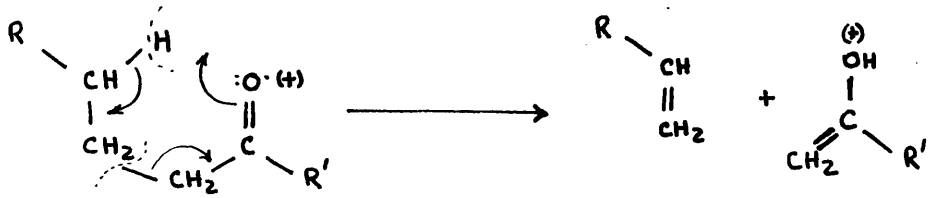
however, this mechanism seems to be in conflict with the behaviour of the carbonyl group in ordinary organic react-:ions (81),ie polarization usually takes place thus:

$$>C=O \longrightarrow C^+ - O^-$$

to give a postive charge on the carbon and a negative on the oxygen ratherthan vice versa:

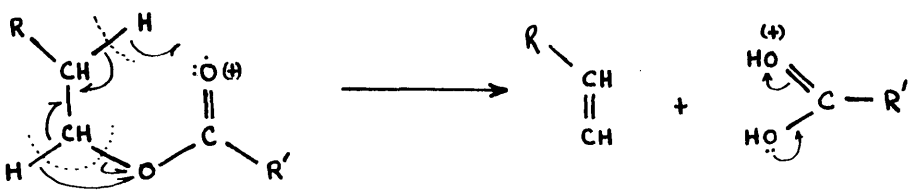
$$>C=O \longrightarrow C^- - O^+$$

which is implied by McLafferty. In addition, if the oxygen atom already possesses a positive charge as in the above example, such back polarization is even less likely. Perhaps a better mechanism would be:



Whichever process is correct, the effects of the electron withdrawing group and also the pseudo cyclic transition com-:plex are clearly shown. Evidence has been obtained (103) from appearance potential studies that the ionic fragment is in the enolic configuration as shown rather than in the alternative ketonic state.

In the cases of esters, amides, phosphates etc. (101, 104, 105) an ion with two hydrogen atoms rearranged is often obtained. A probable mechanism is:



It will be observed that the even electron ion produced is stabilized by resonance, a factor which, together with the possibility of a pseudo-cyclic intermediate being formed, may promote this type of rearrangement.

Relatively few mass spectrometric studies have been carried out on alicyclic compounds containing bridging groups. Spectra of α-pinene, camphene and nor-camphor type molecules have been obtained by Reed and Gilchrist (85) while Reed (84) has also obtained the "cracking patt-:erns" of the two isomeric carenes. In the present work,

an attempt has been made to apply the general principles outlined above to the interpretation of the principle peaks of the mass spectra of camphor and some of its halo-:gen derivatives. It should be borne in mind that only a qualitative account can be given at the present state of our knowledge.

[illegible] plate. Its focussing properties were not adve[illegible]ly affected to any great extent by this technique. [illegible] sample mounted on the tip of a copper rod of somewha[illegible] smaller diameter than the whole in the repeller plate, [illegible] lowered carefully into the ionization chamber until [illegible] material just entered the fringe of the electron bea[illegible] permitted of the formation of a sufficiently high [illegible] of vapour in the ionization chamber without the [illegible] of external heat. The amount of gas could [illegible] if desired by raising the tip of the rod further [illegible] from the vicinity of the electron beam. The sample

Apparatus And Method.

The samples were analysed by volatilizing the solid into the ionization chamber of a Metropolitan-Vickers M.S.2 mass spectrometer which had been modified somewhat to facilitate the handling of solid materials. To allow close approach of the solid to the electron beam, a small hole of about 2mm. dia. was drilled in the centre of the "Nier" repeller plate. Its focussing properties were not adversely affected to any great extent by this technique. The sample mounted on the tip of a copper rod of somewhat smaller diameter than the whole in the repeller plate, was then lowered carefully into the innization chamber until the material just entered the fringe of the electron beam. This permitted of the formation of a sufficiently high pressure of vapour in the ionization chamber without the application of external heat. The amount of gas could be reduced if desired by raising the tip of the rod further away from the vicinity of the electron beam. The sample inlet tube was then hermetically sealed by means of a screw cap and lead washer as described by Reed (83).

The mass spectra were measured at an electron energy of 50 eV. using a stabilized trap current of 100μA. the tube pressure being maintained at 5×10^{-6} mm. Hg. as meas-

:ured by an ionization gauge. Scanning was effected by varying the magnetic field.

Materials.

A sample of purified camphor prepared by Gilchrist (85) was used in this work. Analytically pure specimens of α- and β- bromo-, α-chloro-, β-iodo-, α:α-dibromo- and α:β-dibromo- derivatives of camphor were kindly provided by Dr. J.D.Loudon, of this Department.

	M.A.	M.S.	E.I.	M.N.	E.I.	M.N.
[illegible]	12	93	14	67	21	43
[illegible]	9.3	81	30	55	43	41
[illegible]	37	69	26	53	17	39

2. α-Chloro Camphor.

[illegible]	28	109	24	83	100	55
[illegible]	31	107	19	81	39	43
[illegible]	24	95	21	69	56	41
123	60	93	36	67	33	39

3. α-Bromo Camphor.

232	30	109	9	83	99	55
[illegible]	10	[illegible]	10	[illegible]	43	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	69	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	57	[illegible]	41

RESULTS.

The mass numbers (M.N.) and relative intensities (R.I.) of the more prominent peaks in the mass spectra of the compounds studied are listed in table 19. Owing to the necessity to run the mass spectrometer at its maximum sensitivity, the relative abundances quoted should be considered as approximate (± 20% of the figure given).

TABLE 19

The mass spectra of camphor and some of its derivatives.

1. Camphor

M.N.	R.I.	M.N.	R.I.	M.N.	R.I.	M.N.	R.I.
152	12	83	14	67	21	43	38
109	9.3	81	30	55	43	41	100
95	37	69	25	53	17	39	44

2. α-Chloro Camphor.

188	28	109	24	83	100	55	77
186	31	107	19	81	39	43	73
151	24	95	21	69	56	41	85
123	60	93	36	67	33	39	37

3. α-Bromo Camphor.

232	30	109	9	83	99	55	74
230	30	107	10	81	43	53	26
151	40	95	23	69	44	43	41
123	60	93	10	67	29	41	100
						39	52

4. β-Bromo Camphor.

M.N.	R.I.	M.N.	R.I.	M.N.	R.I.	M.N.	R.I.
232	2	109	66	83	72	55	24
230	2	107	18	81	26	53	22
151	100	95	22	79	16	43	20
123	42	93	18	69	44	41 39	58 56

5. β-Iodo Camphor.

278	3	107	7	81	30	53	17
151	100	95	28	79	8	43	15
123	53	93	7	69	53	41	35
109	73	83	75	55	33	39	18

6. α:α-Dibromo Camphor.

310	4	150	2	55	43	41	30
308	4	122	12	53	18	39	20
201	13	83	100	43	14	-	-

7. α:β-Dibromo Camphor.

310	10	187	24	83	76	55	50
308	12	150	40	81	48	53	45
231	38	122	100	79	48	51	31
229	40	107	29	77	28	43	38
203	21	95	41	69	34	41	95
201	22	93	30	67	17	39	66
189	22	-	-	-	-	-	-

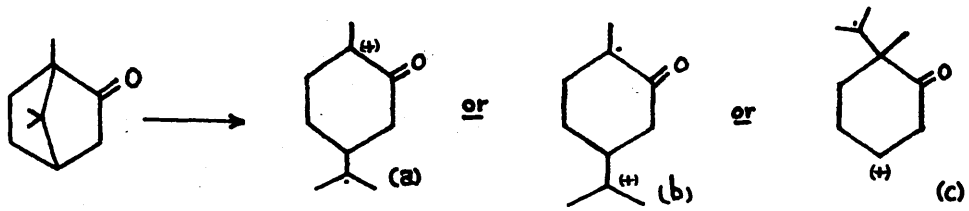
Key: (p) - Parent; (i) - Isotope; (r) - Rearrange-
Ment.

DISCUSSION.

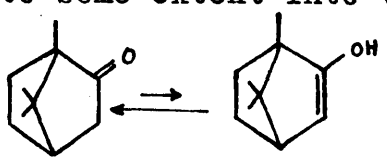
It is now proposed to examine the spectra recorded in Table 19 to discover whether the ions observed are formed in accordance with those general principles out-:lined in the Introduction or whether some further assump-:tions must be made regarding the mechanism of decomposit-:ion of the camphor molecule. It is clear that any set of dissociation processes given should apply in general terms to all the members of the series studied and that any postulates made should not be in serious contradiction with the well known therories of organic reactions. It will be convenient first of all to consider camphor itself, then to discuss the mono- and disubstituted derivatives as two separate groups.

Camphor:

A strong peak occurs at mass number 152. This corr-:esponds with the loss of an electron from the intact molecule. By analogy with the cases of formaldehyde, acetaldehyde and propionaldehyde examined by Reed and his coworkers (53,106,107), the camphor molecule ion could be obtained by removal of a non-bonding electron from the oxygen atom. Alternatively, the strained iso-propylidene bridge may be opened as in the case of α-pinene, camphene and nor-camphor (85).



A factor which may contribute to the formation of (a),(b) or (c) is the possibility that the camphor molecule may tautomerize to some extent into the enol configuration.

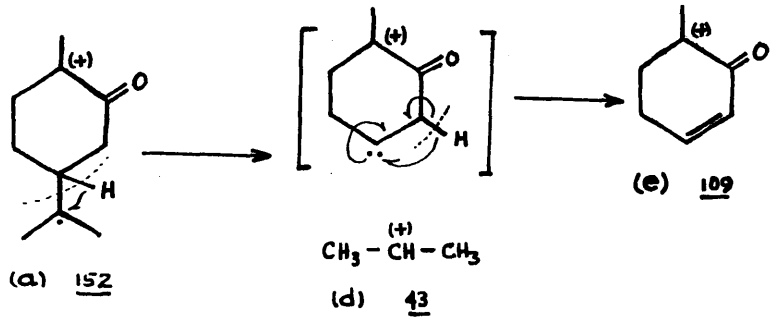


It will now be observed that the bridge bonds are now allylic to the enolic double bond and hence dissociation at these points will be enhanced. It is likely that the α-β bridge bond will break to give (a) or (b) in preference to rupture of the β-γ bond to give (c) above for the following reasons:

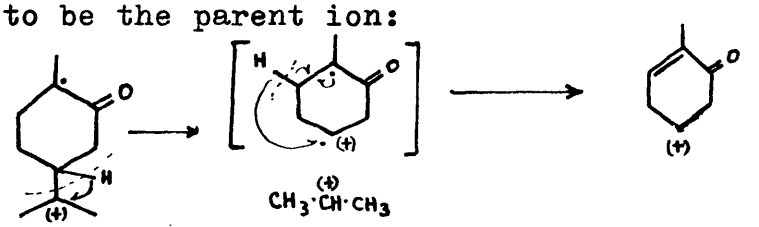
(1) α-β bond scission takes place at a quaternary centre while β-γ does not.

(2) α-β bond cleavage results in the methyl and iso-propylidene groups both being equatorial while β-γ dissociation would require one of these entities to be axial. Hence (c) would be conformationally less stable than (a) or (b) (108).

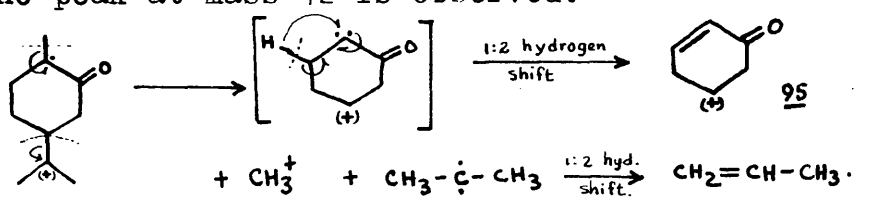
Now that the possibility of formation of (a) and (b) has been established, the ion of mass 109 can be considered to be derived as follows:



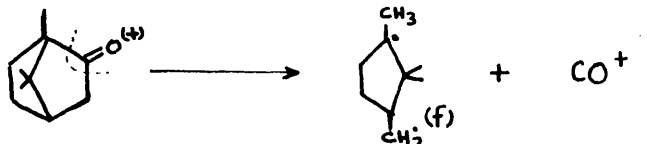
The process involves elision of the iso-propylidene group with simultaneous migration of a hydrogen atom from the alicyclic fragment to give an isopropyl ion (d) of mass 43 and an intermediate which undergoes 1:2 hydrogen rearrange-:ment to give the ion (e) of mass 109. The rearrangement is likely to be promoted by the fact that straightforward cleavage gives odd-electron ions of masses 110 and 42 whose heats of formations are likely to be greater than those of (d) or (e) which contain an even number of elect-:rons. A similar procedure can be postulated assuming (b) to be the parent ion:



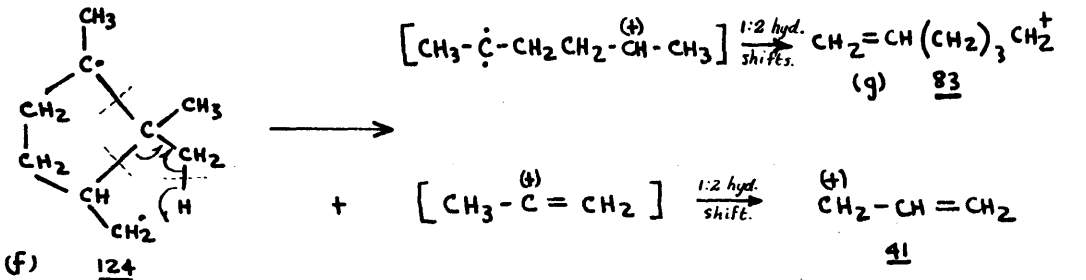
(b) can also be regarded as a possible precursor of the ion of mass 95. In this case, fragments of 15 and 42 mass units are lost from the parent and it is considered that these might correspond to CH_3^+ and $CH_3CH{-}CH_2$, since no peak at mass 42 is observed:

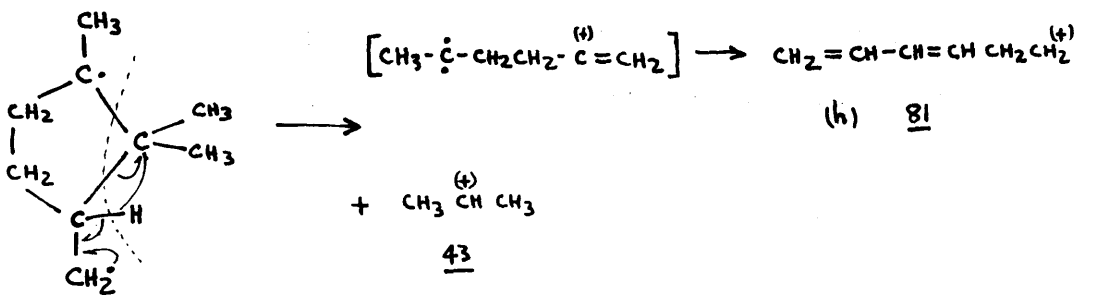


It has been observed by McLafferty (109) and Beynon (110) that ketones readily undergo fission at the carbonyl group. This can be used to explain the peaks at mass numbers 83 and 81. If the camphor molecule ion is assumed to be formed by removal of a non-bonding electron from the oxygen atom, then elimination of CO^+ will probably result in the formation of the diradical (f) of mass 124.



Since no peaks were obtained at mass numbers 124 (corresponding to $(f)^+$) or 62 ($(f)^{++}$), the loss of 28 mass units must take place without further loss of electrons from the hydrocarbon skeleton. It is now proposed that (f) gives rise to ions of mass 83 and 81 as follows:





The intermediates written in the square brackets attain the final configurations shown by means of a series of 1:2 and

1:3 hydrogen migrations. The above dissociative mechan-:isms are suggested by the fact that straightforward elim-:ination of $(CH_3)_2C$ and CO from camphor would yield an ion of mass 82 containing an odd number of electrons. Since large peaks are observed at masses 83 and 81 but only a very small one at 82, rearrangement of one hydrogen atom must take place in each case. This allows the formation of relatively stable even electron ions as shown. It is also significant that whereas the relative intensities of masses 41 and 43 are high, that of 42 (Me_2C^+) is negligibly small.

The remaining ions in the mass spectrum, having masses 69, 67, 55 and 53 can be interpreted in terms of the successive cleavage of CH_2 groups from the ions (g) and (h). Thus we have 83 - 14 = 69; 83 - 28 = 55; etc.

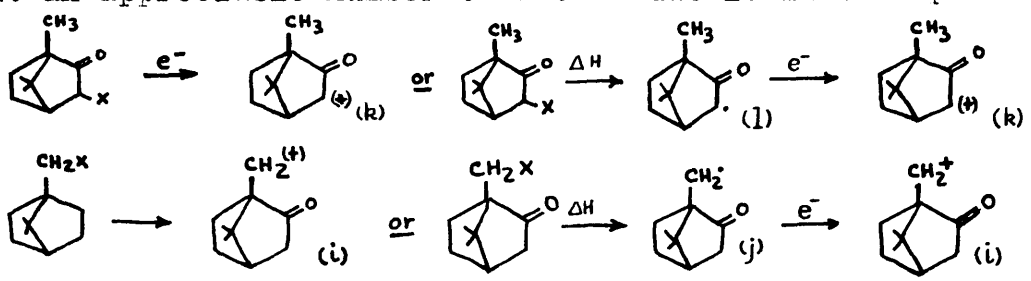
From the foregoing, it can be seen that the behaviour of camphor under electron bombardment tends to confirm the observations made in the Introduction. In particular the great mobility of hydrogen atoms is exemplified. The rearrangements proposed are in keeeping with those class-:ified as "Specific" by McLafferty (91), while the pro-:moting influences of cyclic intermediates and the format-:ion of even electron ions and molecules has been clearly shown.

The Monosubstituted Camphors.

The spectra of the α-substituted compounds show quite

"parent peaks" while those of the β-series are much less marked. Thus the relative abundance of α-$C_{10}H_{15}OBr^+$ = 30% while that of β-$C_{10}H_{15}OBr^+$ = 2% of the most intense ion in the spectrum. On the other hand, the ions of mass 151 which are obtained by dehalogenation of the parent compounds have a higher relative intensity in the β-series than in the α. e.g. in the two cases mentioned, the abundance of 151 is 40% and 100% respectively. This is taken to mean that in the α-series, the C-Br bond is appreciably stronger than in the β-series.

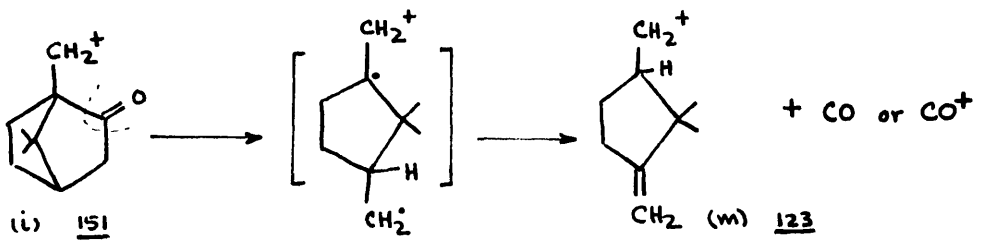
There are two ways in which the ions of mass 151 may arise. The halogen may be lost by direct electron impact or alternatively, the high temperature of the filament (600°C) may cause thermal dissociation of the halogen to give a free radical which subsequently becomes ionised. Examination of the lower molecular weight fragments of the mass spectra will show that both processes are possible and that an appreciable number of free radicals must be present.



Beyond mass number 151, the spectra of the monohalocamphors are qualitatively similar to that of camphor itself. In addition to large peaks at masses 109, 95, 83

and 81, there are some ions which were not obtained in very high yield from camphor. These will be discussed below.

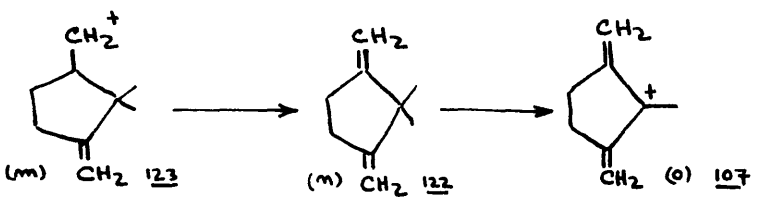
After dehalogenation, the first fragment ion in each spectrum has a mass of 123. This can be regarded as an elision of CO or CO^+ from any of the entities (i) - (l). Taking (i) as an example:



(i) 151 (m) 123

Similarly, the compounds (j) - (l) can give rise either to (m) itself or an intermediate which can readily rearrange to (m) by means of hydrogen migration. In the case of camphor the mass spectrum showed very little trace of a peak at mass 123. This is consistent with the postulated mechanism, since removal of CO or CO^+ would give either an uncharged molecule, a doubly charged molecule or a singly charged ion having an odd number of electrons. Hence the intensity of an ion corresponding to (m) derived from camphor would be much smaller.

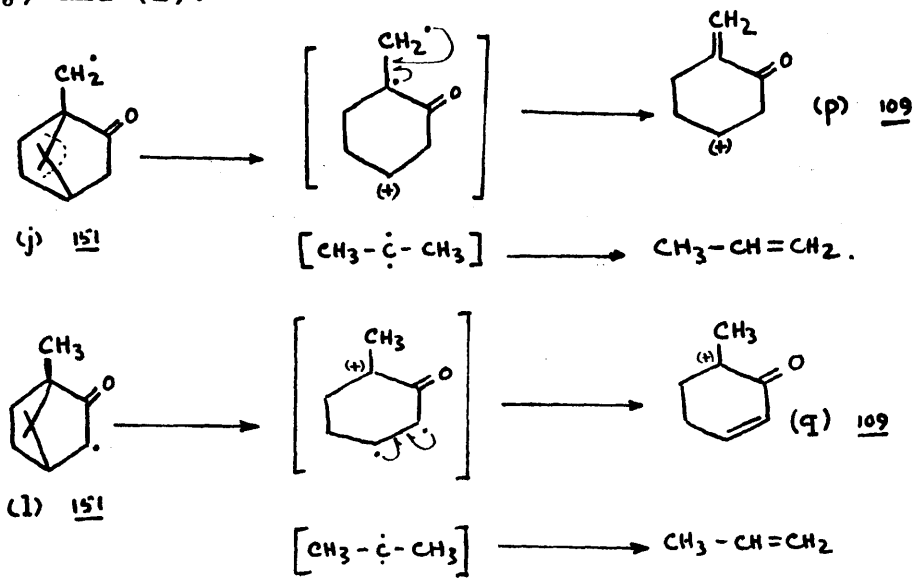
(m) can now eliminate H^+ to produce the diolefin (n):



(n) has a gem-dimethyl group allylic to two double bonds,

hence one of these methyl groups will be very readily el-:iminated to give the ion (o) of mass 107. A fairly in-:tense peak corresponding to 107 is present in all four spectra but since (m) can undergo competing reactions, the relative intensity of (o) will be smaller than would nor-.mally be the case.

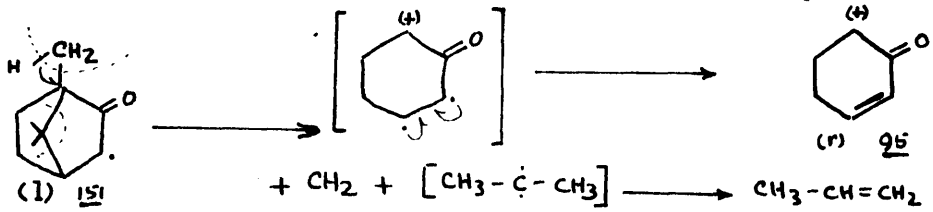
There is a peak corresponding to mass 109 present in all four spectra, but is much more prominent in the β-series than in the α-. It is thought to be obtained by direct cleavage of the iso-propylidene group. Unlike camphor, no hydrogen migration is required to produce a stable ion. It is best considered as being derived from (j) and (l):



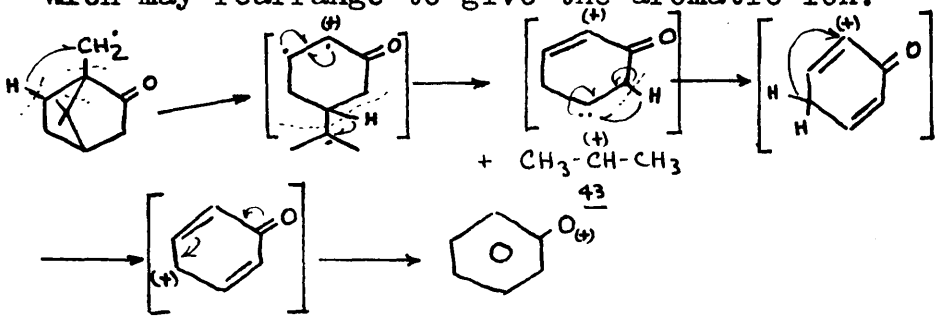
In each case, the end product is an even electron ion having an α:β unsaturated carbonyl system. The fact that this ion is less intense in the α- series than in the β- series may

be connected with the smaller concentration of (1) compared with (j) as mentioned above.

The radicals (j) and (1) may also be considered to be the precursors of the moderately intense ion at mass 95. The mechanism in the case of the β- series is identical with that postulated for camphor itself except that the accompanying single carbon unit is CH_2 rather than CH_3^+. In the α- series, hydrogen migration probably takes place.

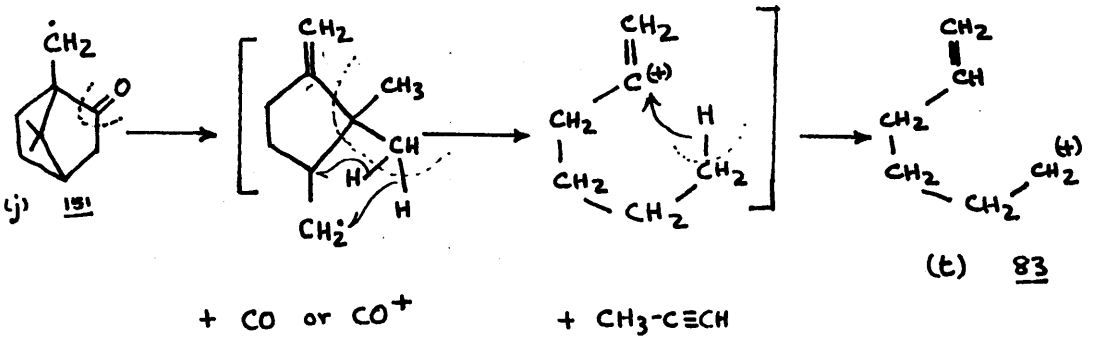


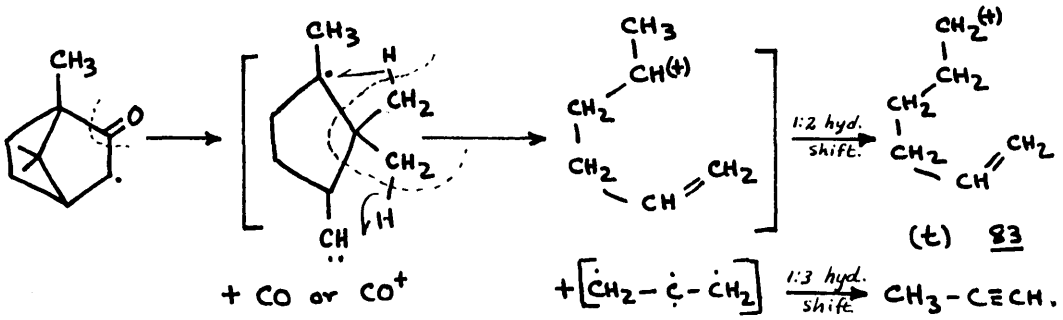
An ion of mass 93 can now arise either from loss of two hydrogens from (r) followed by rearrangement to yield an aromatic ion of the type (s). Alternatively (j) or (1) may rupture in such a way as to produce intermediates which may rearrange to give the aromatic ion.



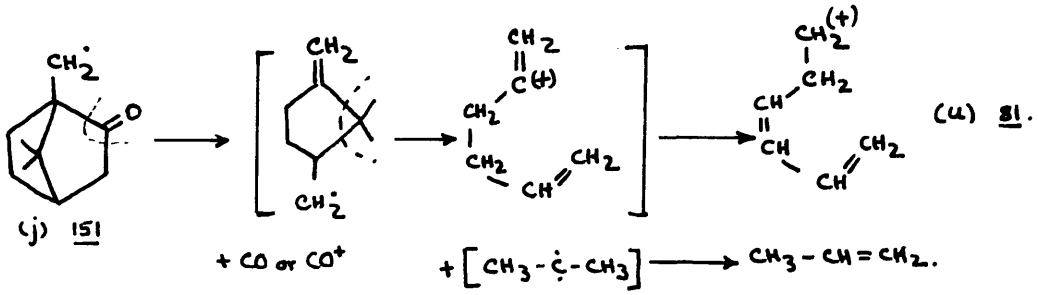
A similar mechanism can be formulated starting from (1).

As in the case of camphor, the ions 83 and 81 are quite prominent. A similar type of decomposition mechan-:ism can be postulated for their formation.





Two hydrogens are thought to migrate from the iso-propylid-:ene group into the six carbon chain to give an intermediate which rearranges to give in each case the ion (t) of mass 83. The accompanying three carbon fragment produced in this mechanism is shown as neutral methylacetylene. This is required since no prominent peak at mass 40 is ob-:seved. If, at the second step in the above processes, straightforward elimination of the iso-propylidene group takes place, then an ion of mass 81 is obtained. The example given shows (j) as the precursor, but a similar process can be formulated for (l).



The final product is probably the conjugated diene ion (u).

The remaining ions in the spectra of the four mono-:halo camphors can be interpreted as the successive fission of CH_2 units from (t) and (u) with the production of ions of masses 69, 67, 55, and 53 all of which are prominent in each spectrum.

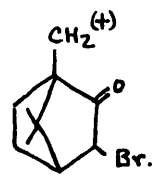
The Disubstituted Camphors.

The mass spectra of both compounds studied have peaks corresponding to the intact molecule ion, but those of the α:α series are much less intense than those of the α:β. This is to be expected on steric grounds, since two bulky bromine atoms on the same carbon represents a relatively unstable system. It is known also from the study of the halogenated methanes (Section 2) that addition of a second bromine to a carbon atom already linked to bromine lowers the C-Br bond energy by 10 - 15K.Cal. Hence in α:α di-:bromo camphor, at least one bromine will be very easily removed.

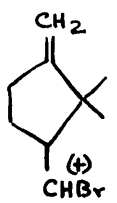
A novel feature of the spectra of the disubstituted camphors, one which was not observed to any appreciable ex-:tent in the study of the monosubstituted compounds or of camphor itself, is the presence of peaks corresponding to fragment ions containing one bromine atom. The ions in question occur at masses 201 for the α:α compound and at 229, 201 and 187 for the α:β derivative, with isotope peaks

of about the same relative intensity at masses 231, 203 and 189 due to the corresponding ions containing ^{81}Br.

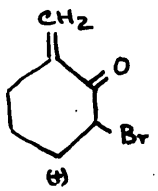
By analogy with previous observations and having re-:gard to the postulate that a bromine atom is less firmly bound to a β- carbon than to an α- carbon, the probable structures of the above ions are:



229 , 231



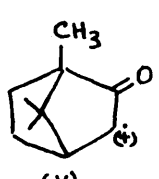
201 , 203



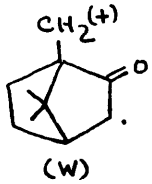
187 , 189

The mechanisms by which these entities arise will be ident-:ical with those already given for the production of the corresponding ions in which hydrogen is substituted for bromine.

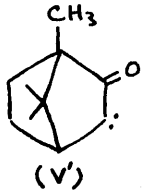
If complete debromination takes place, then a com-:pound of mass 150 is obtained. This is observed in both spectra but the relative intensity of the ion of mass 150 in the case of the α:α dibromo compound is much less than that of the α:β. When the probable structures (v) and (w) are considered:



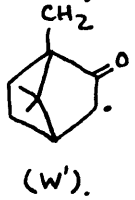
(v)



(w)



(v')

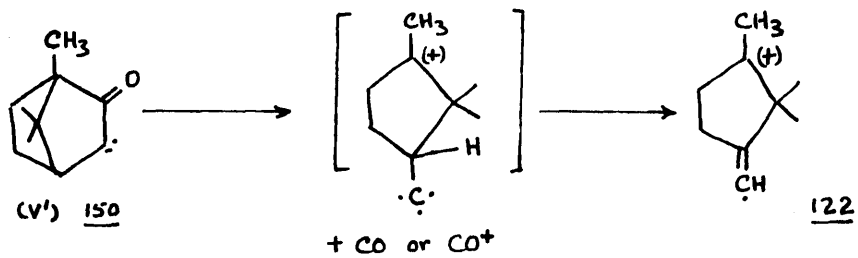


(w').

it is seen that in (v), the unsaturation of the molecule is concentrated on a single carbon atom, while with (w), it is spread over two - which is taken to mean that (w)

will be more stable than (v). As before there is the possibility that the corresponding diradicals (v') and (w') are produced as intermediates in the formation of (v) and (w). The low intensity of (v) may then be explained by the much more rapid decomposition of (v') to give lower molecular weight fragments as compared with ionization to give (v).

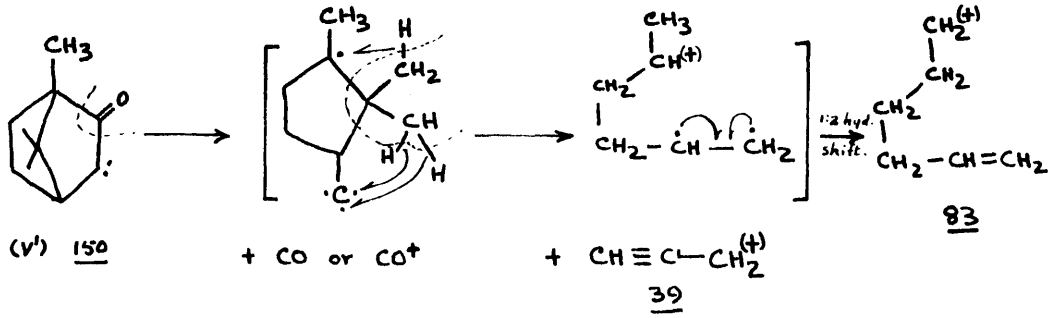
Examination of the spectra below mass 150 shows a marked resemblance to those of the monosubstituted camphors It is therefore likely that the observed ions have struct-:ures identical to those already considered above. Thus an ion of mass 122 could be obtained by cleavage of CO or CO^+ from (v) - - - (w'). For example, starting from (v'):



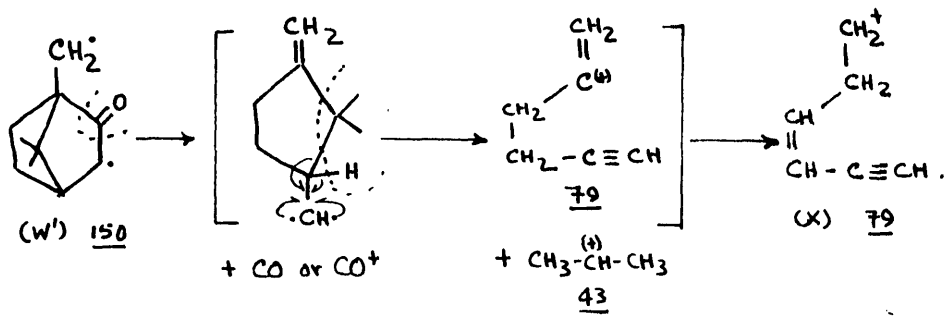
(v') 150 + CO or CO^+ 122

Since the carbon skeleton of (v) - - - (w') contains two unsaturated centres (located either on the same or diff-:erent carbon atoms), a different number of hydrogen mig-:rations will be necessary to produce a given ion compared with the number required to give the corresponding ion from camphor or a monosubstituted camphor. For example, the ion of mass 83, which is the most intense in the spect-:rum of the α:α dibromo derivative, requires three hydrogen

migrations for its formation compared with two in a mono-:substituted camphor and one in camphor itself.



An ion having a mass of 79, not previously noted in any of the spectra discussed, is observed in that of α:β dibromo camphor. It is thought to be obtained from (w') by a similar mechanism to that given above.



Elimination of CO or CO^+ takes place, followed by cleavage of the iso-propylidene group with simultaneous migration of a hydrogen atom from the six to three carbon fragment to give an isopropyl ion of mass 43 and an intermediate which probably undergoes rearrangement to give the conjug-:ated acetylenic compound (x) of mass 79.

Such a mechanism is unlikely to take place in the case of the monosubstituted camphors since the ion of mass 80, so obtained, would have one unpaired electron. With camphor itself, since the precursor (f) has a mass two

units greater than (w'), an identical mechanism would lead to the production of mass 81 as already postulated above.

Conclusion.

As a result of the above observations, it is considered that the ions found in the "cracking patterns" of camphor and its halogen derivatives are produced in accordance with those general principles outlined in the introduction. Plausible mechanisms of bond fission have been put forward based on the current theories of the origin of mass spectra; e.g. facile allylic bond cleavage, ready elimination of CO, etc.

It has also been found that rearrangements of the type classified by McLafferty (91) as "Specific" take place. These, in general, take the form of migrations of one or more hydrogen atoms from one fragment to another or sometimes within a fragment itself. Such rearrangements are considered to be promoted by the difference in energy between the rearranged ion, which usually contains an even number of electrons and the ion obtained by straightforward cleavage, which normally has at least one unpaired electron. These hydrogen migrations are particularly associated with the ready elimination of the iso-propylidene bridge in the camphor derivatives. In some instances the formation of a pseudo-cyclic transition state facilitates a rearrangement. The high mobility of hydrogen atoms observed here is in keeping with the results of other

workers (91).

It should be remembered that although the decomposit-:ion mechanisms discussed above, are plausible, a much more detailed study involving suitably "labelled" camphor deriv-:atives would be required to firmly establish them. How-:ever, since the processes advanced are the simplest which can give rise to the ions observed, and since a single set of dissociative mechanisms can be applied in general terms to all seven spectra obtained, it is concluded that the proposals made in the course of the discussion are reason-:ably well founded and the interpretations of the "cracking patterns" given are fairly close to the truth.

WS/RL.

SECTION 3.

The Electron Impact Studies on Some Chlorobenzaldehydes.

Introduction:

The object of the studies reported here was to in - :vestigate the ionization and dissociation of o-, m- and p- chlorobenzaldehydes and to use a recently determined (112) value of 9.88±0.05 eV. for I(CHO) to obtain estim- :ates of the bond energies $D(R_i\text{-CHO})$ where R_i represents the aromatic fragment. As a check, the appearance and ionization potentials of R_i^+ and R_i were measured and a value of $D(R_i\text{-CHO})$ calculated therefrom.

Benzaldehyde is the only aromatic aldehyde which has been previously studied (107). It is therefore interest- :ing to discover what effect a chlorine atom substituted ortho-, meta- and para- to the formyl group has on $D(R_i\text{-CHO})$ compared with $D(C_6H_5\text{-CHO})$.

EXPERIMENTAL.

The o-, m- and p- chlorobenzaldehydes were reagent grade and were purified by repeated fractional distillat-:ion in vacuuo, the central portion being retained at each stage. Provided the purified samples were kept in the dark at liquid air temperature, no significant oxidation took place between purification and the start of measure-:ments (about 12 hours).

The technique used to obtain the appearance and ion-:ization potentials was identical with that described in Section 1.

RESULTS.

The results obtained in this investigation are listed in Table 20. The uncertainties attached are standard deviations while the units are in electron-volts throughout.

It is convenient to denote the o-, m- and p- chlorophenyl radicals by R_o, R_m and R_p respectively.

TABLE 20

Species	$I(R_iCHO)$	$A(R_i^+)$	$I(R_i)$	$A(CHO^+)$
R_oCHO	9.10 ± 0.05	$\begin{matrix}13.25\pm0.05\\14.15\pm0.05\end{matrix}$	9.4 ± 0.1	13.71 ± 0.05
R_mCHO	9.40 ± 0.05	$\begin{matrix}13.30\pm0.05\\14.33\pm0.05\end{matrix}$	10.23 ± 0.07	12.96 ± 0.05
R_pCHO	9.25 ± 0.05	$\begin{matrix}13.48\pm0.07\\14.61\pm0.05\end{matrix}$	9.6 ± 0.1	13.81 ± 0.05

$$I(CHO) = 9.88\pm0.05 \quad (112)$$

DISCUSSION.

As before, it has been assumed that the fragments produced in the decomposition:

$$e^- + R_x - R_y \longrightarrow R_x^+ + R_y + 2e^-$$

are formed in their electronic ground states. The available test for kinetic energy tends to support the view that the dissociation products possess little or no translational energy, hence in the equation:

$$A(R_x^+) = I(R_x) + D(R_x-R_y) + E_k + E_e \quad (7.1)$$

both E_k and E_e are zero.

By analogy with acrolein and benzaldehyde, (113) it is considered that the least strongly bonded electrons in the chloroaldehydes are the non-bonding electrons of the CHO group and the π- electrons of the benzene ring. Consequently, two possible ionization processes (a) and (b) respectively may be visualized:

$$e^- + R_i - CHO \rightarrow R_i - CHO^+ \rightarrow R_i + CHO^+ + 2e^- \quad (a)$$

$$e^- + R_i - CHO \rightarrow R_i^+ - CHO \rightarrow R_i^+ + CHO + 2e^- \quad (b)$$

where $R_i \equiv R_o$, R_m and R_p. However, since the mobility of electrons between the benzene ring and the formyl group will be very high, it is impossible to say whether (a) or (b) is exclusive or whether both take place simultaneously, but appearance potentials have been observed for R^+ and

CHO^+ in each case. Combination of these with the appropriate ionization potentials in equation (7.1) gives the results quoted in Table 21. (N.B. only the first appearance potential of R_i^+ is considered here; $A_2(R_i^+)$ will be discussed below).

Also, by means of the relationships:

$$A(CHO^+) = I(R_iCHO) + D(R_i\text{-}CHO^+) \qquad (7.2)$$

$$A(R_i^+) = I(R_iCHO) + D(R_i^+\text{-}CHO) \qquad (7.3)$$

it is possible to investigate the effect of removal of an electron on the strength of the R_i- CHO bond. These dissociation energies obtained by substitution in (7.2) and (7.3) are also listed in Table 21 together with $D(C_6H_5\text{-}CHO)$ and $D(C_6H_5\text{-}CHO^+)$ for comparison (113).

TABLE 21.

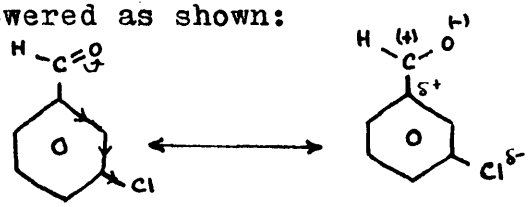
	$D(R_i - CHO)$ eV.		$D(R_i - CHO^+)$	$D(R_i^+ - CHO)$
Species	$A(R_i^+)$	$A(CHO^+)$	eV.	eV.
R_oCHO	3.85±0.15	3.9±0.1	4.61±0.1	4.15±0.1
R_mCHO	3.07±0.12	3.1±0.1	3.56±0.1	3.90±0.1
R_pCHO	3.90±0.15	3.9±0.1	4.56±0.1	4.23±0.1

$D(C_6H_5\text{-}CHO) = 3.7\pm0.3$ eV. $D(C_6H_5\text{-}CHO^+) = 3.96\pm0.22$ eV.

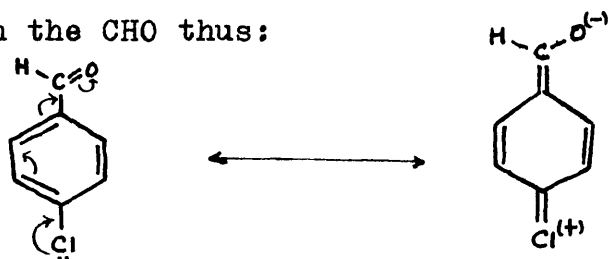
The similarity between the values of $D(R_i\text{-}CHO)$ obtained by the two different methods indicates that the decomposition routes chosen are probably correct. Also, as with acrolein and benzaldehyde, this similarity indicates that the ionization energy levels for the removal of a non-

:bonding electron from CHO and a π-electron from the benz-:ene ring must be close together.

It will be noted that whereas $D(R_i\text{-CHO})$ for the o- , and p- compounds is nearly equal to $D(C_6H_5\text{-CHO})$, $D(R_m\text{-CHO})$ is appreciably less. This may be correlated with the negative inductive effect of the chlorine atom. The chlorine will tend to withdraw electrons from the ben-:zene ring and, coupled with the polarization of the car-:bonyl group, the electron density of the R_m- CHO bond will be lowered as shown:



Hence $D(R_m\text{-CHO})$ is likely to be less than $D(C_6H_5\text{-CHO})$. In the o- and p- compounds, however, the chlorine atom can conjugate with the CHO thus:



Conjugative.

This faculty of electron releasing takes place concurrently with the negative inductive effect, the two processes tend-:ing to oppose one another. The nominal 0.2 eV. difference between $D(R_p\text{-CHO})$ or $D(R_o\text{-CHO})$ and $D(C_6H_5\text{-CHO})$ indicates that the conjugative effect is at least sufficient to overcome the inductive effect. This behaviour is in keeping with the well known (81) effect of chlorine subs-

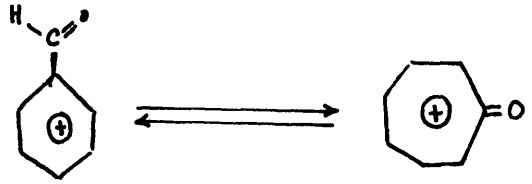
:titution on the strength of benzoic acid, whereby the electron withdrawing properties of a meta-chlorine result in m- chlorobenzoic acid being appreciably stronger than benzoic acid, while the ortho- and para- acids are weaker than the unsubstituted acid owing to the opposing conjug-:ative effect of the chlorine overcoming the inductive.

It is now required to assign $A_2(R_i^+)$ to some suitable mechanism. The differences between $A_2(R_i^+) - A_1(R_i^+)$ are 0.9, eV., 1.03 eV. and 1.13 eV. for $R_i \equiv R_o$, R_m and R_p respectively. It was also found that the number of ions produced at the first appearance potential was unusually small compared with the number found at the second. A similar phenomenon had already been observed for glyoxal, methyl glyoxal and diacetyl by Reed and Brand (112). They considered that the two appearance potentials referred to the formation of neutral CHO radicals in their ground ($^2A''$) and first excited ($^2\Sigma^+$) states togetherwith a pos-:itively charged fragment, R^+, produced in its ground state. Reasons were also advanced by these two workers to account for the abnormally low concentration of ions produced at the lowest appearance potential. The energy separation of these two states of CHO is 1.05 eV. which agrees well with the average observed $A_2(R_i^+) - A_1(R_i^+) = 1.02$ eV. Hence, assuming the production of excited CHO radicals:

$$A_2(R_i^+) = I(R_i) + D(R_i\text{-}CHO) + E \qquad (7.4)$$

where E = 1.05 eV. is the separation of the two energy levels of CHO referred to above. Substitution in (7.4) gives $D(R_o\text{-CHO}) = 3.7 \pm 0.15$ eV., $D(R_m\text{-CHO}) = 3.05 \pm 0.12$ eV., and $D(R_p\text{-CHO}) = 3.96 \pm 0.15$ eV. in good agreement with those values already calculated.

The removal of an electron from R_iCHO has an unusual effect on $D(R_i\text{-CHO})$ as is shown by consideration of $D(R_i^+\text{-CHO})$ and $D(R_i\text{-CHO}^+)$. Normally, when ionization takes place (by loss either of a π- bonding or a non-bonding electron), one expect that the net electron density of the R_i-CHO bond would be lowered somewhat and consequently $D(R_i^+\text{-CHO})$ would be less than $D(R_i\text{-CHO})$ as is the case for the aliphatic aldehydes already studied (107). However, with benzaldehyde and the chlorobenzaldehydes, ionization seems to strengthen rather than weaken the R_i-CHO bond. The reason for this phenomenon is not at all clear. One possibilty is that an electron has been removed from an antibonding orbital (as has been postulated(4) to explain similar behaviour for H_2O, H_2S and NH_3) with resultant stabilization of the parent ion with respect to the molecule. On the other hand, Meyerson and his co-workers (87) have pointed out recently that the benzyl ion seems to undergo ring expansion to give the tropylium ion. Hence it is possible that the benzaldehydes may undergo similar rearrangement to give ionized derivatives of tropone.



If this were the case, the simple relationships given above would be no longer valid. This hypothesis could be investigated by a study of a series of substituted tropones. Unfortunately there has not been sufficient time to procure the necessary materials to carry out such an investigation.

WS/RL.

APPENDIX

Thermochemical Data Used in the Foregoing Sections.

1. Standard Enthalpies of Formation:

ΔH_f (g) (eV.) at 1 atm. and 25°C. CF_4, - 9.45 (115); CCl_4, - 1.06; CBr_4, - 0.39 (117); $CHCl_3$, - 1.04; $CHBr_3$, - 0.4 (calculated from ΔH_f (l.) assuming λ_{vap} = 9.6 kω); CH_2Cl_2, - 0.91; CH_2Br_2, - 0.4; CH_3Cl, - 0.85; CH_3Br, - 0.36; NH_3, - 0.48. Unindexed values are from reference (116).

2. Dissociation Energies:

Dissociation energies (eV.) obtained from the literature (reference (5).) $D(H_2)$, 4.52; $D(F_2)$, 1.65; $D(Cl_2)$, 2.48; $D(Br_2)$, 1.98; D(H-Cl), 4.45; D(H-Br), 3.75. Other dissociation energies have been referred to in the text.

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ACKNOWLEDGEMENTS.

The Author wishes to express his gratitude to Dr. R.I. Reed for his help and encouragement throughout the course of these researches. Thanks are also due to Dr. J.D. Loudon, Mr. T. Gilchrist (of this Department), Mr. E. Schmidt (of the Stern Refrigeration Co. Ltd.), and W.Harris (of Imperial Chemical Industries Limited), for the provision of samples.

To the Technical Staff of the Chemistry Department I would extend my thanks for their assistance in the main-:tainance of the Mass Spectrometer.

The provision of a Maintainance Allowance by the Department of Scientific and Industrial Research during the period of this work is gratefully acknowledged.